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THESIS

EQUILIBRIA IN TWO PHASE, GAS-LIQUID HYDROCARBON SYSTEMS

Turner Valley Mixtures

By A. Gillies and J.T. Hugill

University of Alberta
Edmonton, Alberta April, 1940

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A THESIS

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TURNER VALLEY MIXTURES

University of Alberta,
Department of Chemistry,
April, 1940.

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and
J. T. Hugill, B.Sc.

Under the Direction of:
Dr. E. H. Boomer.

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EQUILIBRIA IN TWO PHASE
GAS-LIQUID HYDROCARBON SYSTEMS

Submitted in Partial Fulfillment
of the
Requirements for the Degree of
Master of Science

by

Archibald Gillies, B.Sc.

and

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Under the Direction of
Dr. E. H. Boomer

Time Devoted to This Work - 10 Months

Edmonton, Alberta. April, 1940.

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EQUILIBRIA IN TWO PHASE, GAS-LIQUID HYDROCARBON SYSTEMS - TURNER VALLEY MIXTURES

INTRODUCTION

The physical behavior of gas and liquid mixtures, either as single phase or two phase systems, has been the subject of a large body of work, the beginnings of which were some fifty years ago. Many investigations are in progress and possibly this type of work is becoming more widespread. The importance of such work lies in the necessity for knowledge of the pressure-volume-temperature composition relations in physical systems for both pure and applied science.

The present project is concerned with one class of substances, the hydrocarbons, and to a large extent with only one type of system, - two phase, gas-liquid, polycomponent. Comprehensive investigations of this type of system are of relatively recent origin and may be considered as having been started only in the past ten years so far as hydrocarbons are concerned. A rapid and continuing growth in the quantity of work being done, however, on the physical behavior of gas-liquid hydrocarbon systems is noticeable by the reports appearing in scientific and technical literature. This growth has been stimulated by the rapid scientific and technical developments during recent years in the industry most concerned, - the petroleum industry.

The investigations reported here are part of a project that has been going forward more or less continuously since 1931. Previous work was concerned with relatively simple two-component systems (3, 4, 5, 6, 7), while the current work deals with complex systems of many components. While investigations of two-component systems could be continued almost indefinitely, it was felt that extension of the work to more complex systems could be made with profit at this time. The primary stimulus to this work lies in the existence of proven oil and gas fields in Alberta about which information is sought that will lead to their proper operation and economic exploitation. This information is obtained by duplicating in the laboratory, so far as is possible, the conditions in the underground reservoir of an oil or gas field, and determining the composition and properties of the phase or phases present.

Chief interest lies in the gas phase in contact with a liquid phase, and in the gas dissolved in the liquid phase. Miller(27) has pointed out clearly in his pioneer report, the important role played by natural gas in the production of petroleum. The type of information being obtained finds use also in other applications. It is becoming increasingly common in industry to employ pressures out of the ordinary range, for specific purposes. This is particularly true of the petroleum industry, where gas-

liquid hydrocarbon systems are processed in large amounts at high pressures. The use of Raoult's and Henry's Laws for design purposes was justified with low or moderate pressures. However, at high pressures, deviations from these ideal laws become too great to warrant their use and resort must be made to direct experimental measurements.

On the purely scientific side, the information obtained enables conclusions as to the validity of suggested equations of state to be drawn, or may lead to the development of suitable new expressions. Data on the behavior of the systems investigated can be expressed in the usual impirical fashion by fugacities and activities and discussed or correlated in the light of the large body of such information now available. Confirmation, for example, with gaseous hydrocarbon mixtures of Lewis' fugacity rule(21), would be of considerable practical and theoretical value.

This report presents the results of preliminary experiments with a natural gas-naphtha system produced from a gas phase well in Turner Valley, Alberta. An apparatus and procedure have been devised to permit quantitative control and examination of the system in equilibrium. The temperature, pressure, and relative amounts of gas and liquid may be varied at will. The densities and phase compositions for one temperature over a range of pressures up to 90 atmospheres with correspondingly increased amounts

of gas have been determined for the two phase system. In addition, the results of much accessory work are given in the body of this report and as appendices. Preliminary to examination of the phases, the physical properties of the materials used were determined and methods of analysis developed. These include the pressure-volume-temperature behavior of the natural gas and the calculation of fugacities.

Further, there is presented a description of the construction, operation and results obtained with a new apparatus for the analysis of hydrocarbon gas mixtures by low temperature distillation. The results show the apparatus to have distinct and marked advantages over those developed and used elsewhere. Finally, there is presented data and discussion on the measurement of the average molecular weight of naphtha fractions by a cryoscopic method and the correlation of the molecular weight with density and refractive index. It will be shown that knowledge of any one of these properties will give the other two within the limitations of the experimental method imposed.

LITERATURE REVIEW

Until the last five years the literature on the type of work presented in this investigation was of considerable age, and somewhat scanty. Furthermore, little or any of the work was done on chemically related substances. In the past few years considerable work has been reported on the solubilities of hydrocarbons.

Johnson(18) gives a very complete review of the literature covering nearly all the solubility work reported. It is proposed in this report to review only the literature dealing with hydrocarbon systems and restrict the major portion of this to more recently published papers.

Possibly one of the earliest studies is that of McDaniel(26). He made a comprehensive study of the solubility of hydrocarbon gases in various organic liquids at atmospheric pressure and over a range of temperatures. His conclusions were borne out by later work. Difficulty was noted in considering the total pressure in relation to the gas pressure and he concluded that Dalton's law of partial pressures did not hold for mixtures of gases and vapours, that the system was not ideal, and that the gas laws did not hold at one atmosphere.

Among the earlier workers on the solubilities of natural gas in various crude oils, the work of Mills and

Heithecker(28) might be mentioned. They reported that the increase in volume of the oil and decrease in the specific gravity were proportional to the amount of gas dissolved. Beecher and Parkhurst(2) and Dow and Calkin(15) added to the results of Mills and Heithecker by showing that the solubility of natural gas decreased with increasing temperature. Lindsay(23) confirmed these results in a rough way from data obtained under field conditions.

Frolich et al (17) studied the solubility of methane in several solvents and presented some interesting conclusions. They state that Henry's law is applicable over a wide pressure range if no chemical compound is formed and derive a practical rule that the solubility of a gas of the vapour type is a linear function of pressure up to one-half to two-thirds of its saturation point at that temperature.

The American Petroleum Institute is sponsoring a series of investigations on Phase Equilibrium in Hydrocarbon Systems. Sage and Lacey(34) have carried out a most comprehensive series of investigations. Their first investigation deals with the system methane-propane and they report regions of retrograde condensation - that is, the phenomenon of transfer of vapour from the liquid to the gas phase - occurring with increased pressure at constant temperature. In addition, increased temperature lowered the critical pressure. From their work on the solubility

of dry natural gas in crude oil, Sage et al (36), point out that equilibrium is reached by a process of mutual interchange of the constituents between the gas and liquid phases. This will be shown more clearly from a discussion of the results of the present investigation. Sage and Lacey also point out that changes in the gas composition affect the solubility. This was noted by Johnson(18). In further studies on the solubility of propane in various oils by Lacey et al (37), the solubility of propane was found to increase rapidly as its partial pressure approached the vapour pressure of pure propane. This is also true of the apparent specific gravity of the dissolved propane.

Considerable study has been done in this laboratory by Boomer and Johnson(8). They investigated two phase two component hydrocarbon systems of which the gas was essentially methane plus some nitrogen, and the liquids were pentane, hexane, heptane, methyl cyclohexane, benzene and toluene. They draw several important conclusions from the results. Assuming the gas behaves as if alone, all liquids in each system studied show negative vapour pressures, which is impossible, and indicates that Dalton's Law does not hold even approximately for mixtures. The actual vapour pressures of the liquid were about one-quarter of those calculated from their concentrations in the gas phase by the ideal gas laws. It was shown that the critical

pressure of the system increased with increased structural and boiling point differences between methane and the liquid in the order pentane, hexane, heptane, cyclohexane, methyl cyclohexane, benzene and toluene. The nitrogen present with the methane tended to distribute in favour of the gas phase at lower pressures and the distribution became more uniform as the pressure increased. This fact will be shown in the results of the present investigation. It was also noted that the temperature had little effect on the phase density except at higher pressures where the system is approaching the critical state. Henry's Law is obeyed up to certain pressures but is far from true above these pressures. The deviation is a function of the critical pressure of the mixture and of the difference between the critical temperatures of the two components. Regions of retrograde condensation are shown in the phase composition - pressure curves, and are greater the greater the difference between the critical temperatures of the components.

Matheson and Cummings(25) studied the vapour pressures of low boiling point hydrocarbons in absorber oil, and show that the vapour pressures exhibit a wide deviation from Raoult's Law. Lewis and Luke(22) with reduced P-V-T relationships show curves for a correction factor to the gas laws applicable to hydrocarbons with more than three carbon atoms per molecule. Corrections were also made to a generalized fugacity plot.

Katz and Hachmuth(19) studied the equilibrium constants in the system crude oil-natural gas over a pressure range from 1 atmosphere to 3,000 pounds, and temperature range of 40° - 200° F. They show the equilibrium constants for methane, ethane, propane, butane, pentane, hexane and heptanes-plus, as converging towards one at the critical pressure. At every temperature studied the equilibrium constant for methane shows a steady decrease to the point of convergence. The other gases show a decrease to a minimum and then an increase to the same point - the minimum being at a progressively lower pressure the heavier the hydrocarbon. They point out also that the concentrations and chemical composition have considerable effect on K values of methane and heptanes-plus.

Scheeline and Gilliland(43) carried out investigations on the equilibrium in the system propane-i-butylene. They endeavour to correlate the values of K as calculated from the mol fraction with those obtained by the ratio of the fugacities from the proposals of Lewis(22) and Brown(11), using Lewis' fugacity rule(21). Considerable difference was found between the two values, especially in the critical region - the experimental values being greater in every case.

Allied to the solubility investigations, considerable data has been presented recently on the pressure-volume-temperature relations of paraffin hydrocarbons.

Brown et al (11) and Selheimer and Brown(43) presented the first comprehensive data collected from the results of previous workers. They have correlated existing data by reduced equations of state from which P-V-T relationships can be estimated over the range not covered by experimental data. The results, while reasonably close for engineering purposes, are not exactly true for all ranges covered. Further data is presented on fugacities and equilibrium constants in the form of graphs based on reduced relations.

Newton(29), from the P-V-T data of many workers, presents data on the activity coefficients of several gases as a function of the reduced temperature and pressure. The activity coefficient is defined as the ratio of fugacity to pressure, and is shown to be a function of the reduced temperature and pressure only. Newton and Dodge(30) enlarge on these results in their appliation to the effect of pressure on homogeneous chemical equilibria. They show remarkably good agreement between calculated and observed values.

Edminster(16) gives a wide rang of thermodynamic properties of methane as calculated from the data of previous workers, notably that of Kvalnes and Gady(20). From the values of residual volumes as a function of temperature and pressure, C_p, C_p-C_v, the Joule-Thompson coefficient and entropy can be derived using suitable equations.

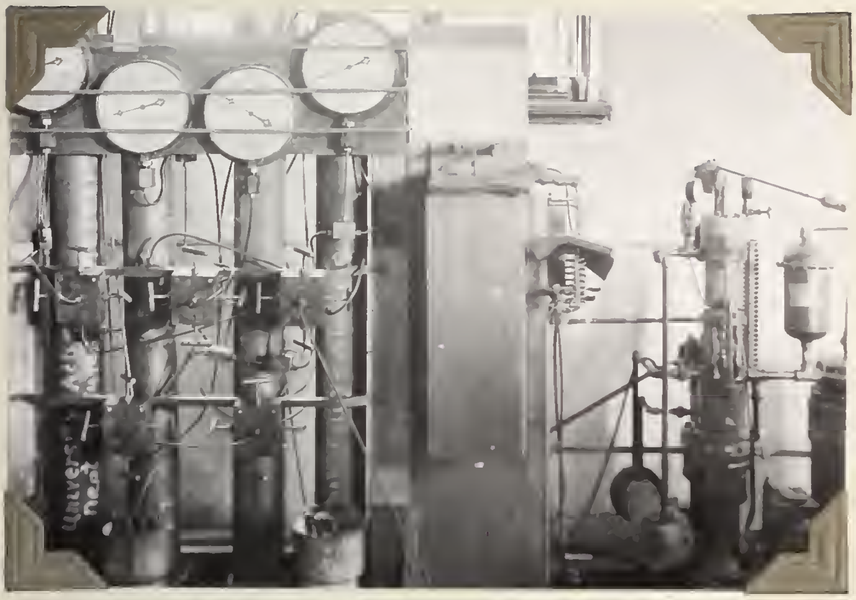

FIGURE 1 : The Main Gas Storage System and Compressor

Sage and Lacey (38, 39, 40, 41) have studied the thermodynamic properties of the first five members of the paraffin series and considerable experimental data are presented. In a later paper(42), the equilibrium of the system methane-ethane is investigated and compressibility factors, partial volumetric behavior, enthalpy-pressure coefficients and partial thermodynamic properties reported for a wide range of temperatures and pressures. They state that the specific value of any of the thermodynamic properties of the whole system may be ascertained from the relation

$$G = \overline{G}_1 n_1 + \overline{G}_2 n_2 - - - -$$

knowing the respective partial quantities.

An extensive investigation is made into the partial volumetric behavior of the lighter paraffin hydrocarbons by Sage and Lacey(43). From experimental data on two component systems of methane and of ethane, propane and n-butane respectively, the authors derived an equation for the specific volume of a complex gaseous mixture using the partial specific volume data of the two component systems, the weight fraction of each gas from analysis and the average mol weight from analysis. They give comparative figures to show the agreement between experimental and calculated results over a wide pressure range and for several temperatures.

In a very recent paper, Budenholzer, Sage et al (13) present a study of some of the thermodynamic properties of the system methane-n-butane. Data on the Joule-Thompson coefficients and heat capacities for several mixtures are shown as a function of temperature and pressure.

MATERIALS

The naphtha and gas used in this investigation were obtained from Royalite Well Number 27 in Turner Valley, Alberta. The well produces 2,737,000 cu. ft. of gas measured at 60° F. and 14.4 lb. pressure, and 5 barrels of separator naphtha per twenty-four hours. The gas was taken directly from the well head (51°F.) into pressure bombs of 1 cu. ft. capacity under 600 pounds per square inch pressure. The naphtha was taken from the separator at the well (100° F. and 330 lbs. per square inch pressure).

In order to remove sulphur compounds from the gas and naphtha, and also to reduce the pentane content of the gas, both materials were passed through a scrubbing system. The scrubbing apparatus, essentially the same as that used by Piercey(31), consisted of a four-foot glass-packed column filled with 20% NaOH, ice-water, and ice-salt condensers, a charcoal adsorber and a naphtha receiver. The outlet of the apparatus was connected to a gasometer. The pressure bomb was connected to the bottom of the column, the valve slightly opened and the gas and naphtha allowed to expand into the system. The pentane, which had been adsorbed by the charcoal, was stripped from it using steam at about 300° C. and added to the naphtha. The gas was passed through a calcium chloride drier and compressed into the main storage system (Fig. 1).

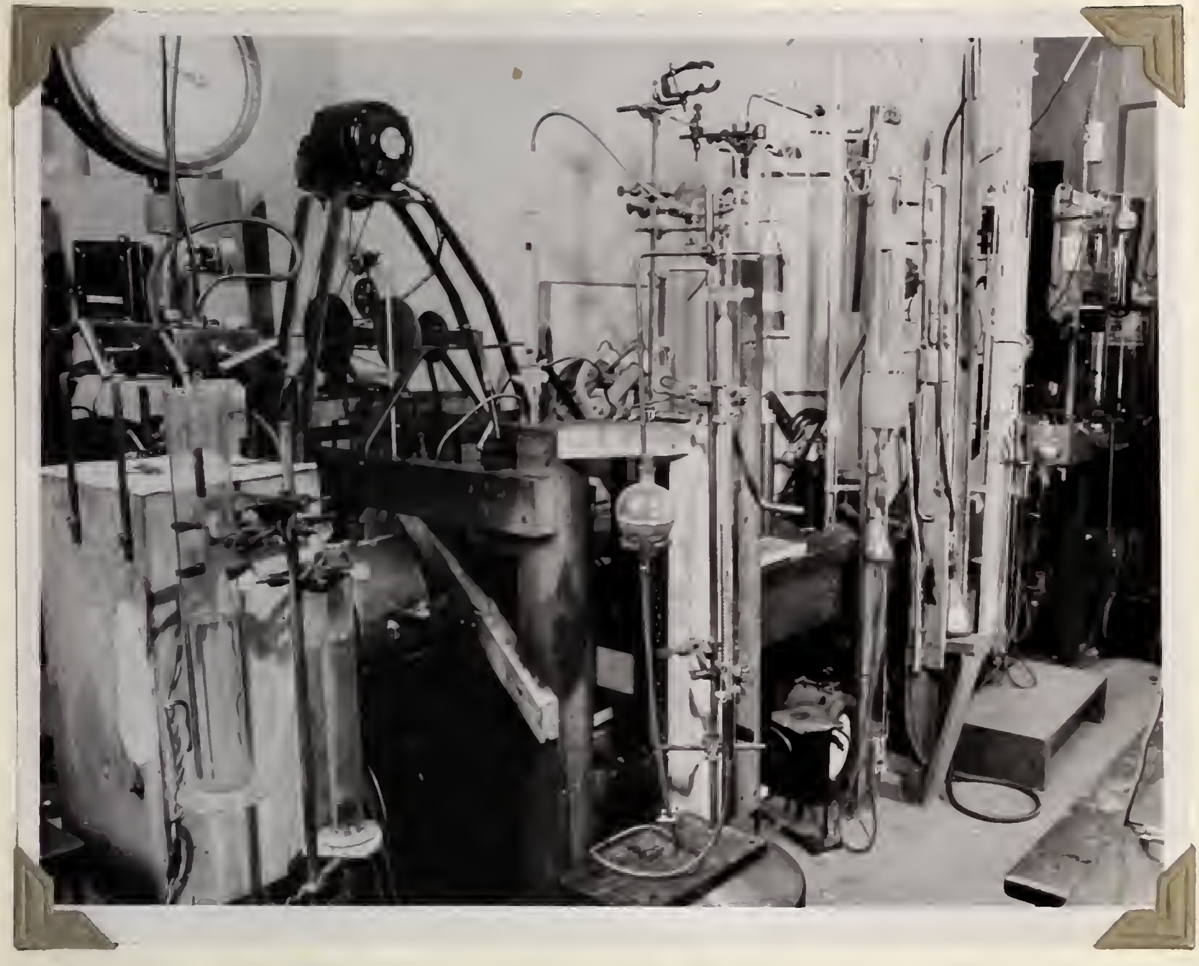

FIGURE 2 : The Experimental Apparatus showing the High Pressure System on the left and the Analytical Apparatus on the right.

The physical properties and composition of the materials were then determined (Appendices I and II).

The density of the naphtha was determined gravimetrically and the value $d_4^{20} = 0.7009$ used in calculations. The refractive index was 1.3955 and the mean molecular weight 93.7. A precise fractionation of the naphtha was carried out and the following results obtained:

Cut	Temperature Range °C.	Vol. %
1	to 40	17
2	40 - 55	18
3	55 - 68	19
4	68 - 75	5
5	75 - 80	12
6	Residue	29

This represents the average obtained by plotting four runs and determining the best line through the points. The first cut is pentane, the only one which is of specific interest at present in this project.

For the purpose of correlating the physical properties of the naphtha as well as of condensates obtained in the main project, an A.S.T.M. distillation was carried out on the naphtha, and physical properties of the fractions determined.

Fraction	Temperature Range	Vol. c.c.	Ref. Index	Density	Mean Mol. Weight
1	to 70° C.	20	1.3826	0.6726	87.5
2	70- 81° C.	20	1.3880	0.6839	90.5
3	81- 90° C.	20	1.3945	0.6972	91.5
4	90- 98° C.	21	1.4007	0.7104	93.1
5	98-110° C.	21	1.4087	0.7259	99.8
6	110-150° C.	18	1.4208	0.7481	111.5

Residue - 1 c.c.
Loss - 4 c.c.

The density of the Royalite gas was determined by weighing a calibrated bulb containing the gas measured at a definite temperature and pressure. The result of many determinations, none of which differed greatly from the mean, gave the average value of $d^{25}_{76} = 0.8006$~~,~~ litre

Samples of the gas were analysed by means of the low temperature-low pressure fractionating apparatus and the following composition found:

Component	Volume %
Methane	79.57
Nitrogen	5.00
Ethane	9.47
Propane	4.03
Butane	1.56
Pentane +	0.37

The nitrogen content was determined by combustion analysis of the methane-nitrogen fraction.

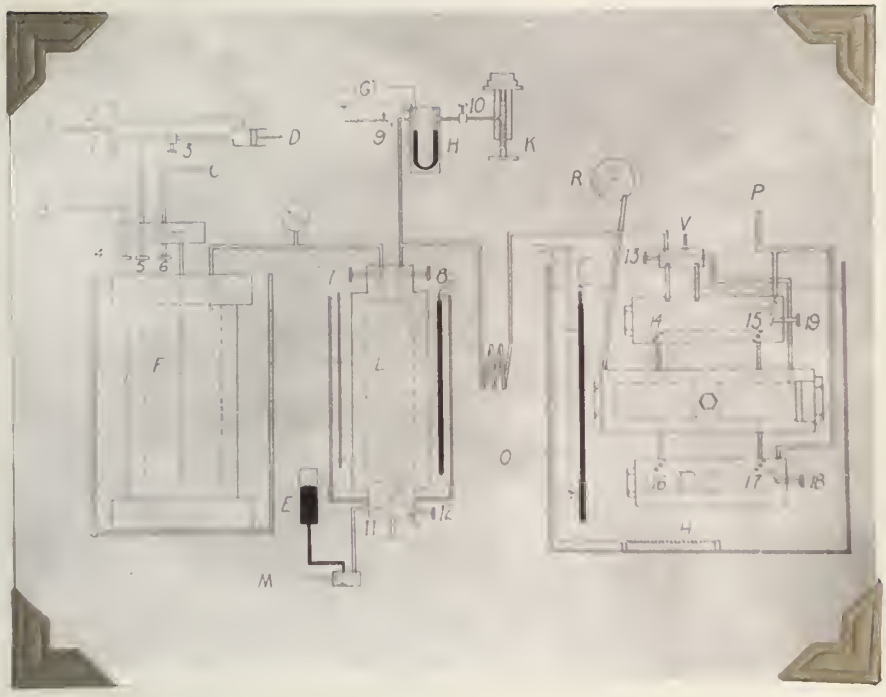

FIGURE 3: Diagram of the High Pressure Solubility Apparatus

APPARATUS

The apparatus can be divided into four parts:

1. High pressure storage and solubility system.
2. Low pressure analytical system.
3. The naphtha dispensing burette.
4. The naphtha fractionating column.

The high pressure storage and solubility apparatus is shown in Figure 3. It consists essentially of a storage vessel F, a gas measuring pipette L, and the solubility pipettes. Royalite gas is admitted at A from the high pressure storage system (Figure 1) through valve 1, direct to the heated storage vessel ~~E~~ F, or through valve 2 to the Booster compressor D and valve 3 to vessel ~~E~~ F. The storage vessel is equipped with 3 valves which are respectively - valve 5, for Royalite gas; valve 4, for Viking gas from line B; and valve 6, to the atmospheric line C. The vessel is one-third filled with $CaCl_2$ and enclosed in a wooden box equipped with a 400 watt electric heater. The outlet line to the measuring pipette has a Bourdon gage connected to it. The measuring pipette L is provided with two needle valves 7 and 8. A hydraulic pump M with a mercury reservoir E is connected at the bottom through valve 11 and a discharge valve is provided at 12. The

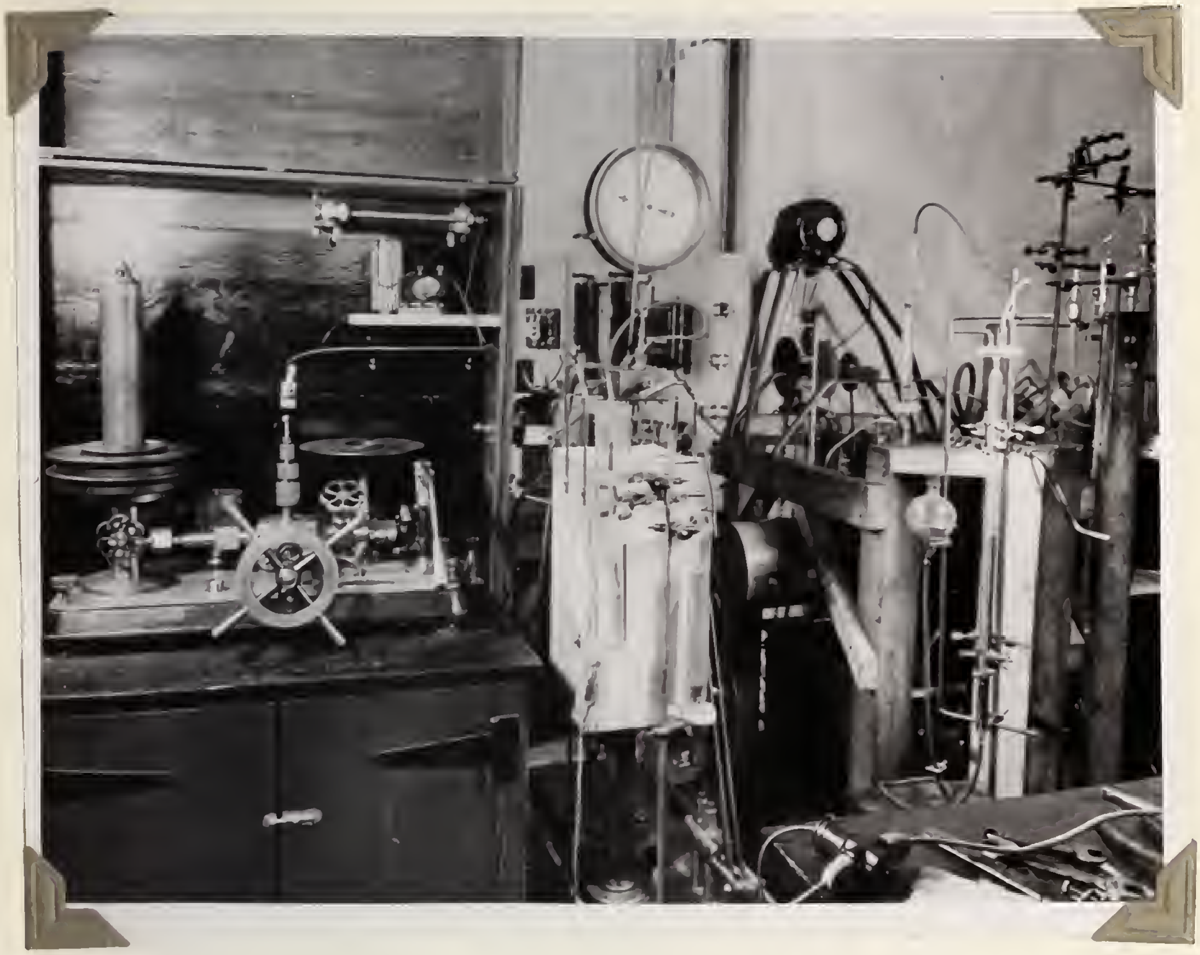

FIGURE 4: The High Pressure Apparatus.

pipette L is immersed in an electrically heated oil bath, maintained thermostatically at a constant temperature of 60° C ± 0.15° C.

A connection from the outlet line is made to the deadweight piston gage K, through the steel U-tube H containing mercury. The U-tube is fitted on the gas leg with a small blow-off valve 9 and an insulated lead terminating in a platinum point at the level of the mercury. A small current, provided by a dry-cell and rheostat, registered on the galvonometer G when contact with the mercury was made or broken and thus indicated the level of the mercury. The oil leg of the U-tube was connected to the piston gage through 1/8 inch tubing and the valve 10. This mercury seal was essential in preventing solution of the gas used in the castor oil of the piston gage.

The outlet line from the pipette L is connected through a flexible copper coil to the inlet valve 13 on the solubility pipettes. This valve is fitted with a standard taper, steel, male connection that will take the naphtha measuring pipette to be described. The bore of the connection is threaded and has an internal seal to fit a hardened steel closure plug.

The solubility apparatus consists of an upper and lower pipette connected to two central chambers through valves 14 and 15 and 1/16 inch tubing, and valves 16 and 17 and 1/8 inch tubing respectively. Outlets to the analytical

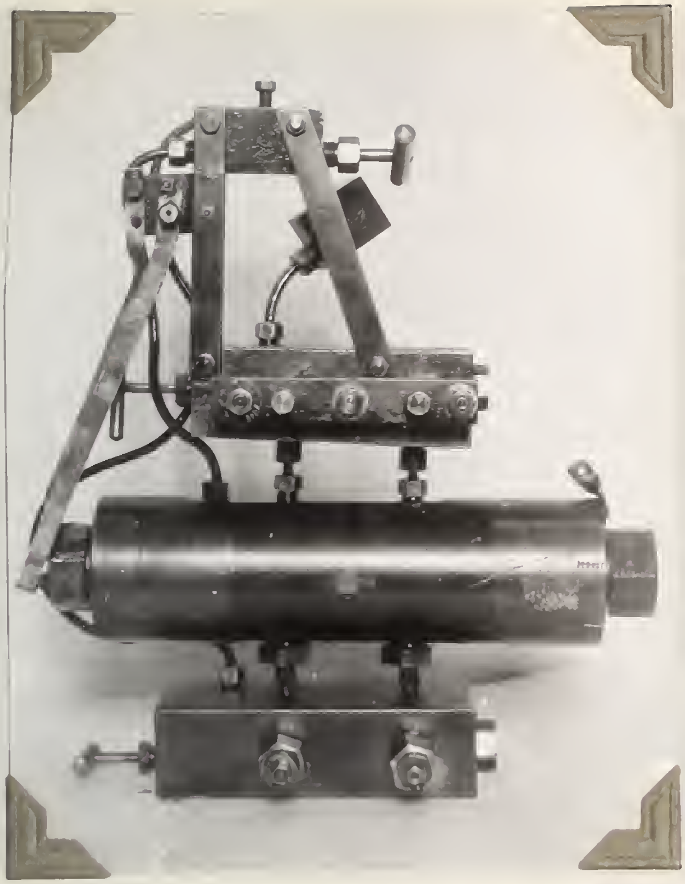

FIGURE 5 : The Solubility Pipettes,

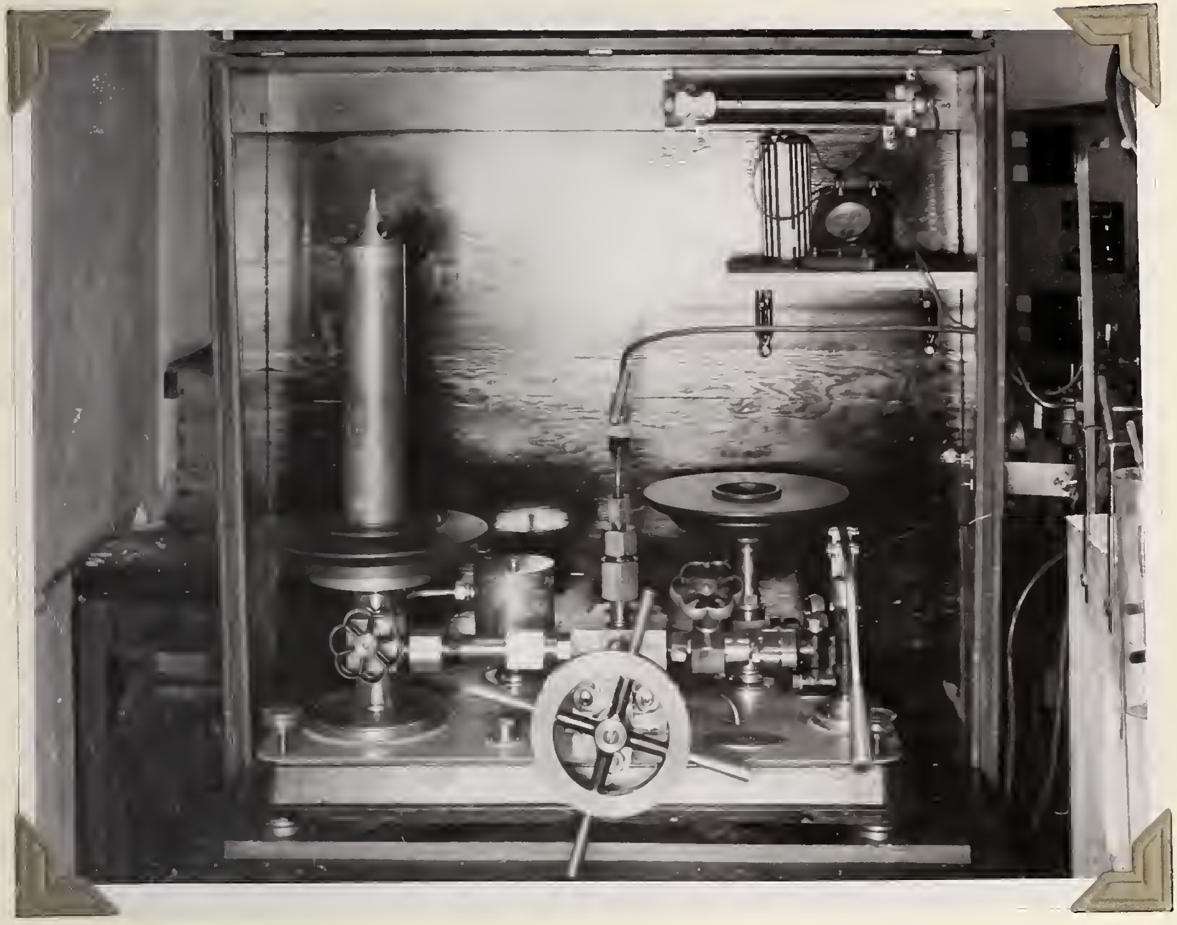

FIGURE 6; The Dead Weight Piston Gage.

apparatus are made through valves 18 and 19 to P. The lower pipette has a ball and piston machined to a slightly smaller diameter than that of the chamber. These slide freely and ensure constant mixing of the liquid and its transfer to the central chambers. The whole assembly is immersed in an oil bath O equipped with a stirrer and a 400 watt thermostatically controlled open heater H. A 400 watt auxiliary strap heater on the outside of the bath was used for rapid heating. The temperature, controlled to 0.1° C, was read on a calibrated thermometer. A mechanism providing oscillation of the whole pipette assembly transmitted motion through a connecting rod attached to the end of the central reservoir. This oscillation promoted equilibrium and shortened the time necessary to reach it. The mechanism and reasons for its use are described in detail by Boomer et al (4).

The analytical apparatus (Figure **9**) is essentially the same as used by Johnson(18), and Piercey(31), with modifications and additions required for operation on complex mixtures. It falls into three main groups - the condenser train, the measuring system, and the fractionating column assembly. The apparatus is all glass except for certain metal parts and is designed for high vacuum operation.

Connection is made to the solubility pipettes from line P (Figure **3**) through a metal to glass connec-

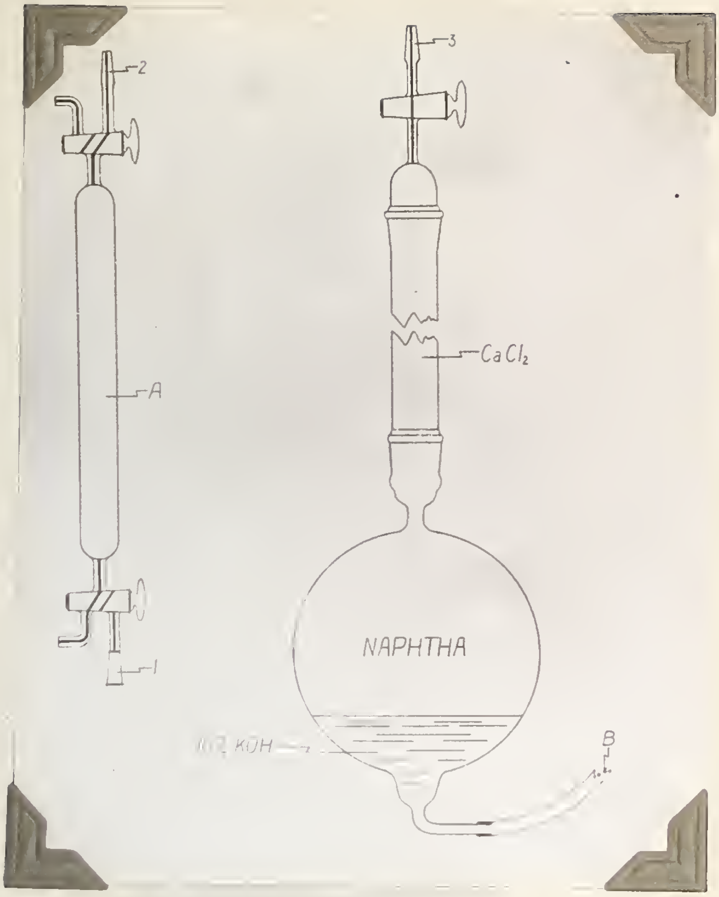

FIGURE 7: Diagram of the Liquid Sample Burette and the Naphtha Dispensing Apparatus.

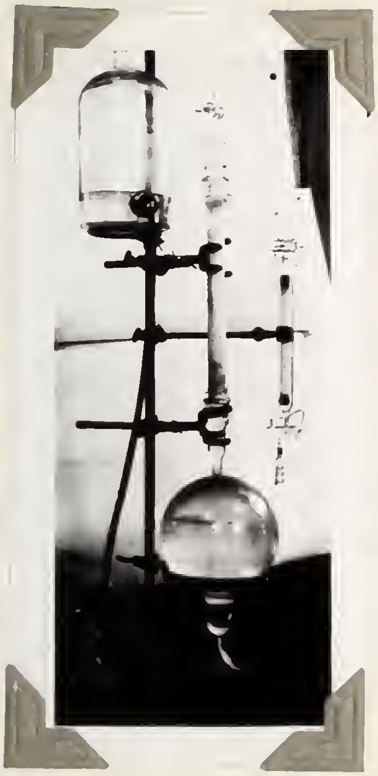

FIGURE 8: The Naphtha Dispensing Apparatus and the Liquid Sample Burette.

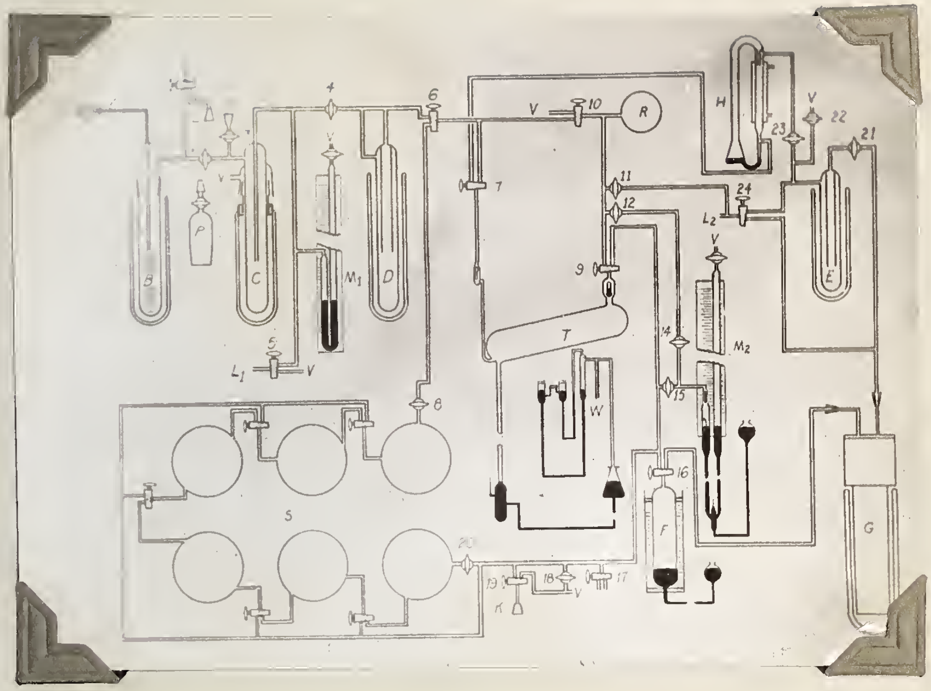

FIGURE 9: Diagram of the Analytical Apparatus.

tion A (Figure 9). The pressure tubing is soldered into the metal block and the glass capillary tube fitted in and sealed with sealing wax. Condensers are shown at B, C and D - B and C being equipped with double junction, Copper-Constantin thermocouples. Condenser B consists of a graduated receiver fitted to a ground glass joint on the apparatus. This condenser also fits cap P which can be placed on the apparatus at L for evacuation through stop cock 1 which leads to the vacuum pumps. The ground glass connection O and stop cock 3 can be used for introducing or withdrawing gas samples when necessary for special purposes. Condenser C is sealed in a short outer tube carrying a vacuum connection and terminating in a ground joint that fits a ground joint inserted in the stopper of a Dewar flask, as shown. This Dewar flask is filled with a solid carbon dioxide-acetone mixture which provided a constant temperature of -112° C. when vacuum was applied. The outlet of condenser C was connected to manometer M_1 and via the two-way stop cock 5 to the McLeod gage at L_1 and through stop cock 4 to the third condenser D. From the condenser D, the two-way stop cock 6 connects the condenser train through stop cock 7 to the intake side of the Toepler pump T and also to the measuring bulbs S.

The entire measuring system is calibrated and consists of six one-litre bulbs, each of known volume,

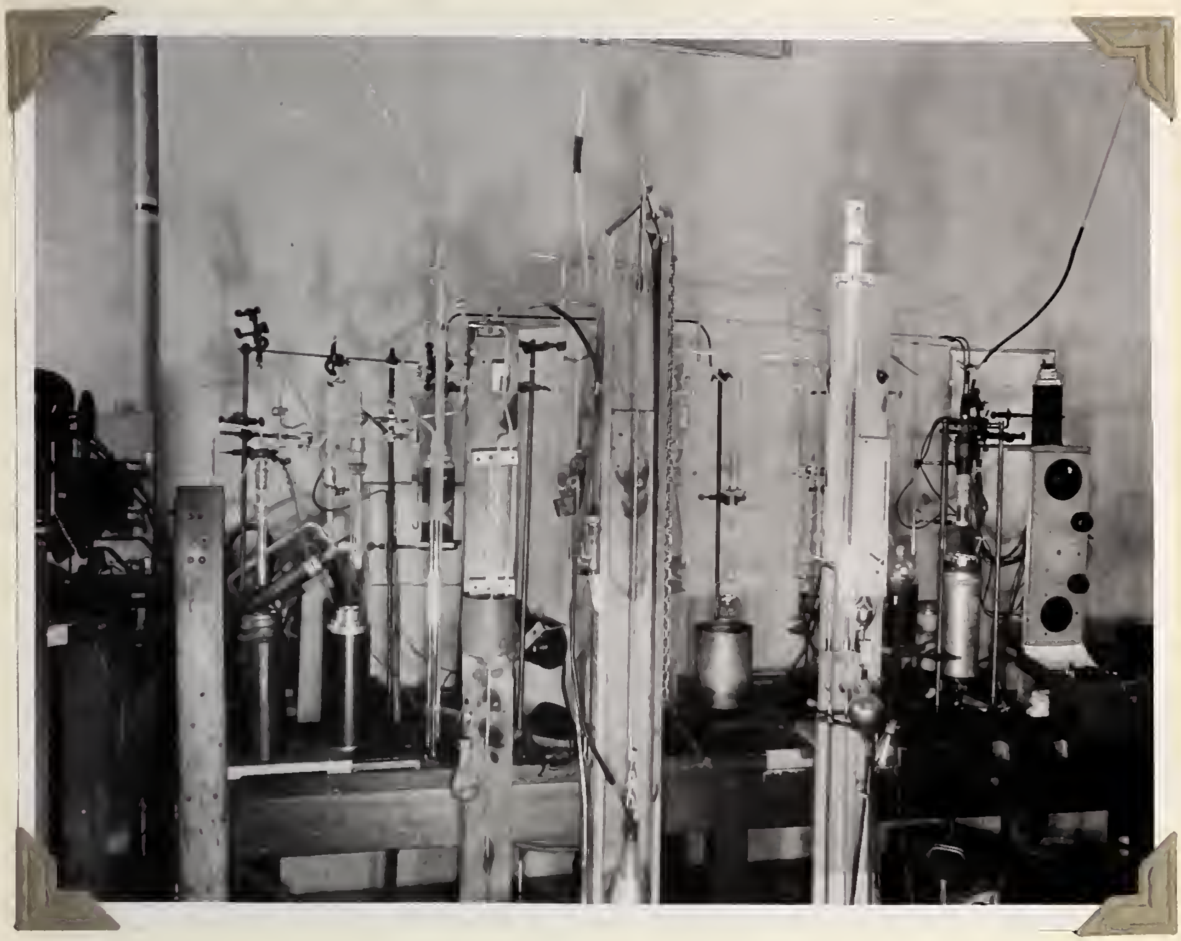

FIGURE 10: The Analytical Apparatus.

connected by a circulating system to the Toepler pump and to a constant volume precision manometer M_2. They are all mounted within an enclosed air bath in which uniform temperature is maintained by a fan. The bulbs are arranged with two-way stop cocks outside the air bath so that each can be opened to the circulating system, or into each other. The whole measuring system is built in such a way as to reduce dead space to a minimum and ensure circulation of all the gas in the system. On the circulating line are outlets to atmosphere and to the precision combustion apparatus at stop cock 17 and to the vacuum pumps at stop cock 18. A ground glass joint K permits a gas density bulb of 530 c.c. volume to be connected through two-way stop cock 19 to the circulating system and to the vacuum pumps.

The manometer is equipped with a mirror glass scale and can be read to 0.2 mm. The scale was found to be sufficiently accurate on comparison with a precision cathetometer. The Toepler pump can be operated automatically up to 20 cm. back pressure by the device (24) connected to the water pump at /.

The fractionating column assembly consists of a calibrated sample burette F in a water jacket connected to the circulating system and to the column by stop cock 16. The vapour outlet from the column G leads to a liquid air trap E, then through stop cock 22 to a dif-

FIGURE 11: Diagram of the Naphtha Fractionating Column.

fusion pump H and thence through the Toepler pump to the fraction receiver R. This receiver is inside the air bath surrounding the measuring bulbs. A McLeod gage at L_2 can be connected to the outlet from the column or to the outlet from the liquid air trap E and to the fraction receiver as required by operation of stop cocks 10 and 11. The precision manometer M_2 may be isolated from the gas measuring system by stop cock 12 and connected to the fraction receiver through stop cock 14.

The vacuum sides of both manometers are provided with connections to the vacuum pumps as are also both McLeod gages. The pumping system consists of mercury diffusion pumps, backed by a Hi-Vac pump.

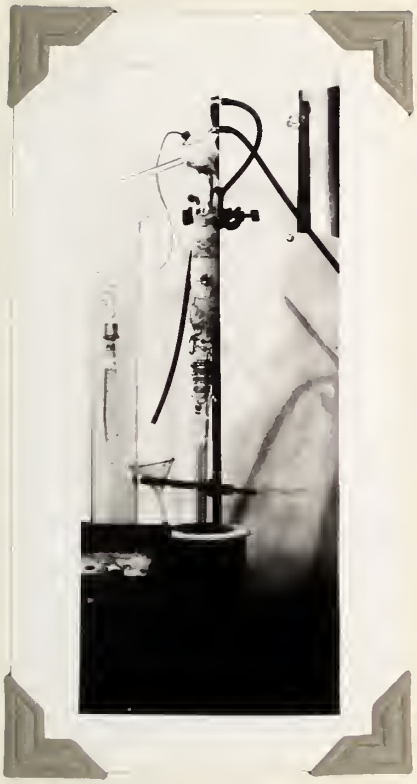

FIGURE 12: The Naphtha Fractionating Column.

PROCEDURE

Any residue of naphtha in the central chambers of the solubility pipettes was removed by flushing with a stream of Royalite gas. Valves 18 and 19 (Figure 3) were then closed and the pressure in the pipettes left at 1 atmosphere. The stop cocks of the liquid sample burette (Figure 7) were lubricated with a gel made from mannitol and glycerol (insoluble in naphtha) and the burette evacuated. It was then connected to the top of the naphtha storage system and the air in the connecting tube forced out by naphtha. Naphtha was then admitted to the burette until 50 c.c. had been obtained. The burette was removed and weighed.

The burette was then transferred to the standard taper connection on the valve V of the solubility pipette assembly. With the lower stop cock on the naphtha burette connecting the solubility pipettes to atmosphere, a little gas was passed through the pipettes to flush out the connecting tube. With the stop cock closed, the pressure in the pipettes was reduced to about 0.5 atmosphere. The naphtha was then run into the pipettes and Royalite gas admitted through the upper stop cock of the naphtha burette to flush the burette and bring the pressure in all the apparatus to 1 atmosphere. The burette was then removed and weighed. The inlet

through the standard taper connection was closed with its steel plug. The volume of gas admitted with the naphtha was added to the volume of gas represented by the half atmosphere pressure in the pipettes and recorded.

The thermostatically controlled temperature of the mercury pipette L (Figure 3) was maintained at 60.0 ± 0.15 degrees Centigrade. With valve 8 open, the pressure of the gas in the pipettes was adjusted to the desired value as measured on the dead-weight piston gage K.

The pipettes in the oil bath were thermostatically maintained at 25.0 ± 0.1 degrees Centigrade. Valve 13 was opened and mercury pumped into the pipette L until the pressure reached that desired. Valve 13 was then closed and the pipettes rocked for ten or fifteen minutes. The pressure was then tested and more mercury pumped in until the pressure was again that required. This was repeated until three successive tests showed no fall in pressure. Equilibrium was then assumed to have been attained. The oil bath was lowered and valves 14, 15, 16 and 17 closed, thus isolating a gas phase sample in the upper pipette and a liquid phase sample in the lower pipette.

Removal of Contents of Lower Pipettes

All necessary parts of the analytical and storage system (Figure 9) were evacuated. A Dewar tube containing a mixture of solid carbon dioxide and acetone at a tempera-

ture of -79° C. was raised in position to cool condenser B. Condenser C was also surrounded by carbon dioxide in acetone and the pressure over the mixture was reduced with a resulting lowering of the temperature to -112° C.

When the temperatures had been established, the outlet valve 18 of the lower pipette was opened carefully and the gas-liquid mixture allowed to escape to the condenser train at a rate of about 100 c.c. (at one atmosphere) per minute. Most of the liquid contents and some of the gaseous components in the phase sample were retained in condenser B. By careful adjustment of tap 4, the uncondensed gas was admitted at a fairly uniform rate to the gas measuring system, while the Toepler pump was operating.

After expansion of the phase sample was complete, the gas was pumped off until the remaining pressure was 1 cm. of mercury. Condenser D was then surrounded by liquid air and pumping continued. Pentane distilled over from B to C and butane and lighter gases into D. Pumping was continued until the pressure was 0.15 mm. of mercury as measured on the McLeod Gage L_1. In this way the pipette was completely emptied and a separation of its contents into liquid and gas portions obtained. Condensers B and C contained only pentanes and heavier hydrocarbons, while condenser D contained butanes and lighter hydrocarbons with traces of pentanes. With tap 4 closed

and the liquid air removed, the contents of condenser D were evaporated and pumped into the gas measuring system. The total volume, pressure and temperature were recorded. This gas was then circulated for sufficient time to ensure uniform composition throughout. Duplicate density determinations were made by means of a 530 c.c. density bulb attached at K. Samples were also taken for duplicate fractional distillation analysis as described in Appendix I.

While the density sample was being taken, the density bulb was surrounded by an air bath. The temperature of the bath was read on a calibrated thermometer and recorded. The pressure was read on the constant volume precision manometer L_2, the temperature of the mercury was also read and these data recorded. The grease was removed from the ground glass joint of the bulb using benzene. The bulb was carefully wiped and hung on the balance long enough for uniform temperature to be established before being weighed. The balance case contained a small amount of pitchblende which readily destroyed any static charge on the bulb due to wiping. The evacuated bulb was handled in the same manner and was weighed frequently, and always re-weighed when operators changed.

The acetone-carbon dioxide mixtures were removed from condensers B and C and condenser B immersed in liquid

air. The liquid in C distilled back into B. Upon standing, this became solid; air was admitted and the condenser removed. The cap P, previously greased and weighed, was fitted to the condenser and the latter evacuated by attaching it at L. It was then removed from the liquid air, allowed to warm up to room temperature, and weighed. The refractive index of the liquid was determined and the pentane distilled off and measured (Figure 11). The refractive index, density and molecular weight of the residue was determined.

The procedure for removing the contents of the gas phase pipette was the same as that just described. In the pressure range used, only minute amounts of pentane and heavier hydrocarbons were found in the gas phase sample. These were not sufficient to permit refractive index or distillation determinations.

RESULTS AND DISCUSSION

The experimental results and their discussion will be presented in two principal parts. There will be given first the pressure-volume-temperature behavior of Royalite gas, and second, the behavior of the two-phase equilibrium system.

Pressure-Volume-Temperature Behavior of Royalite Gas

In order to have complete information as to the behavior of the natural gas used in this work and as a matter of interest to know the fugacity of the gas as a function of pressure, the pressure-volume behavior was determined at two temperatures , 25° C. and 60° C. , and pressures from about 15 cm. of mercury up to 173 atmospheres.

In measurements above 1 atmosphere one of the solubility pipettes was used to provide a known volume of the gas at 25° C. and 60° C. as required, and at a pressure determined precisely by the dead weight piston gage. This sample of gas was allowed to expand into the measuring system (Figure 9) and was transferred completely by means of the Toepler pump. The volume of gas in the measuring system, its temperature and pressure, was recorded. A volume was chosen so as to give a pressure of the expanded gas as close as possible to 70 cm. of

TABLE 1

Pressure-Volume-Temperature Data * on Royalite Gas

Pressure		25°C.		60°C.	
p.s.i.	atmos.	PV/P_0V_0	density	PV/P_0V_0	density
113.6	7.73	-	-	1.111	0.0056
213.6	14.56	-	-	1.096	0.01063
213.6		-	-	1.097	-
313.6	21.34	0.9492	0.01701	1.0855	0.01575
313.6		-	-	1.0811	0.01581
513.6	34.95	0.9132	0.03066	1.0560	0.02651
713.6	48.56	0.8779	0.04431	1.0300	0.03776
1013.6	68.97	0.8266	0.06684	0.9970	0.05543
1263.6	85.98	0.7875	0.08746	0.9718	0.07088
1513.6	102.99	0.7556	0.1092	0.9459	0.08723
1763.6	120.01	0.7352	0.1310	0.9343	0.1029
2013.6	137.02	0.7183	0.1528	0.9232	0.1189
2263.6	154.03	-	-	0.9175	0.1345
2513.6	171.04	-	-	0.9178	0.1492

* This data incorrect. See Boyer or Morrison, Master Thesis, 1941 University of Alberta Library.

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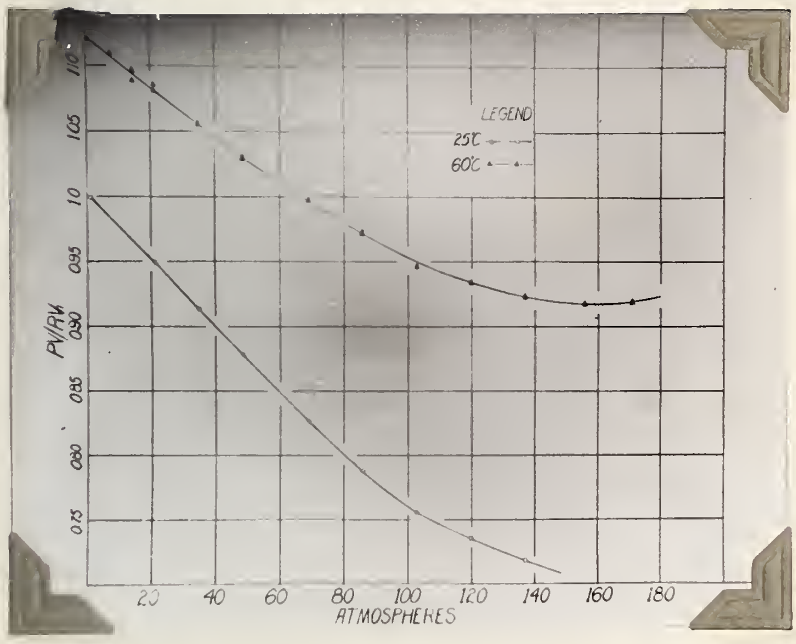

FIGURE 13: The Variation of the Compressibility Factor $PV/P_{\rho}V_{\rho}$ for Royalite Gas.

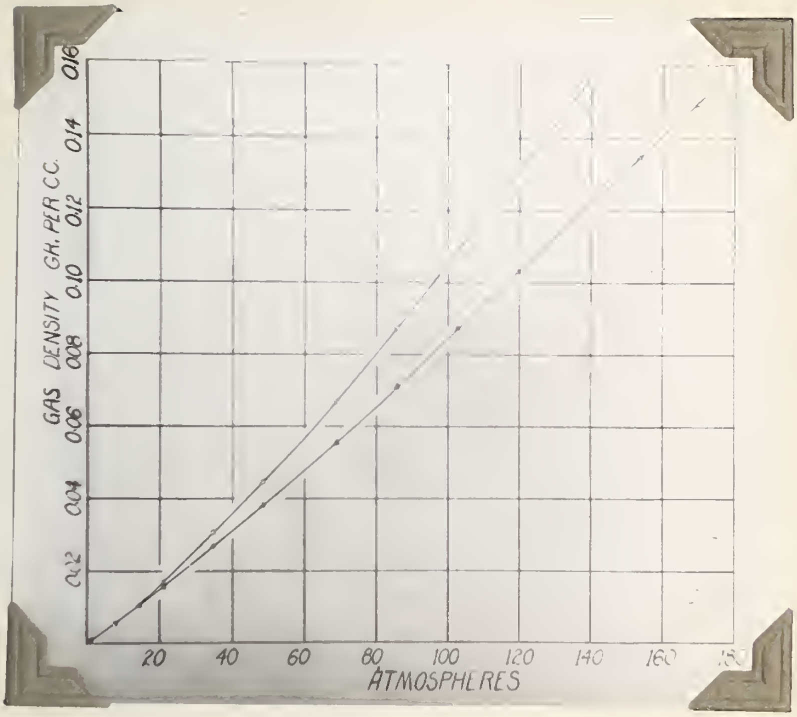

FIGURE 14: The Density-Pressure Relationships for Royalite Gas.

Legend

25°C. ○——○——○

60°C. △——△——△

mercury. The temperature was that of the room, between 20° C. and 25° C. generally. Finally, density determinations were made on the gas and a sample taken for precision analysis in the low temperature-low pressure fractionating column (See Appendix 1).

From the experimental data, the volume of the expanded gas (V_1) at 25° C. and 76 cm. of mercury (P_1), and its mass, were calculated. The pressure-volume product, PV, of the gas in the pipettes before expansion was obtained from the pipette volume and the dead-weight piston gage setting. The ratio of the two products PV/P_1V_1 shows the deviation of the gas from its behavior at 25° C. and 1 atmosphere. The density of the gas in the pipettes before expansion was calculated from the mass of gas and the pipette volume. The results are shown in Table 1 and graphically in Figures 13 and 14.

The residual volume is defined by the equation

$$V = (RT/P) - a$$

From the phase densities at 60° C. as a function of pressure, the values of "a" could be obtained. As the value of "a" depends on the difference between two numbers large scale plotting was used both for the phase density and "a" as a function of pressure. The resulting curve of "a" against P was integrated graphically.

From the equation

$$\ln f/P = -1/RT \int_0^P a\,dP$$

TABLE 2

Fugacities of Paraffin Hydrocarbons

60°F

Pressure		Fugacities, p.s.i.				
p.s.i.	atmos.	CH_4	C_2H_6	C_3H_8	C_4H_{10}	C_5H_{12}
300	20.41	293	269	210	86	32
500	34.02	480	415	240	91	34
700	47.63	635	560	255	96	37
1000	68.05	933	656	274	105	40
1250	85.06	1145	722	291	112	42
1500	102.07	1355	776	308	120	45
1750	119.08	1555	825	326	128	48
2000	136.09	1755	876	346	136	53
2250	153.1	1946	926	367	144	58
2500	170.1	2130	975	388	152	62

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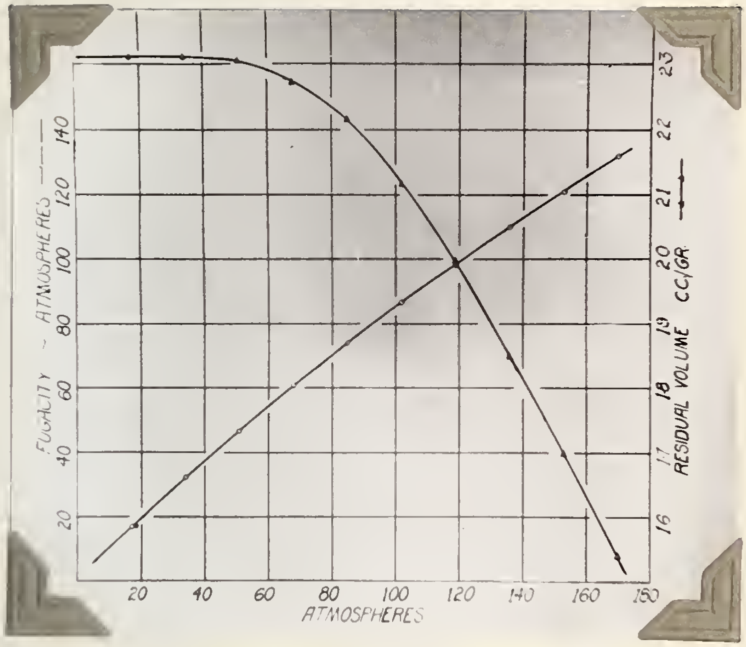

FIGURE 15: The Effect of Pressure on Fugacity and Residual Volume.

Legend

Fugacity at 60°C. ——O——O

Residual Volume at 60°C.——Δ——Δ

TABLE 3

Residual Volumes and Fugacities 60° *

Pressure		residual volumes, ccm/gr.	fugacities		
p.s.i.	atmos.		experiment	Lewis rule	diff.
250	17.01	2.310	16.96	-	-
300	20.41	-	20.70	19.30	1.40
500	34.02	2.310	32.16	31.12	1.04
750	51.03	2.306	46.90	-	-
1000	68.05	2.272	60.83	59.01	1.82
1250	85.06	2.216	74.01	72.83	1.19
1500	102.07	2.116	86.55	84.49	2.06
1750	119.08	1.998	98.54	96.53	2.01
2000	136.09	1.849	110.11	108.62	1.49
2250	153.1	1.698	121.34	119.68	1.66
2500	170.1	1.540	132.31	131.47	0.86

* In error. See Boyer or Morrison, Master Thesis, 1941
U. of T. Library.

and the values of "a" and "p" for pressure ranges of 250 pounds, log f/p and hence f at 60° C. could be calculated. Figure 15 shows "a" and "f" as functions of pressure and the data for these graphs are given in Table 3. The working graph, from which the data were taken, was on a much larger scale than shown in Figure 15.

In order to test Lewis' fugacity rule, fugacity data for the individual hydrocarbons present in the natural gas were obtained from the papers of Sage and Lacey (38, 39, 40, 41, 42). Their values were plotted on a large scale as a function of pressure for two temperatures 130° F. and 160° F. and interpolated to obtain values at 60° C. (140° F.). These values are shown in Table 2. The fugacity of nitrogen was determined from the data of Deming and Shupe (14). This is not shown in Table 2.

The average of several analyses of the natural gas gave the following composition:

Gas Component	Mol. Fraction Present
Methane	0.7957
Nitrogen	0.0500
Ethane	0.0947
Propane	0.0403
Butane	0.0156
Pentane +	0.0037

The fugacity of the Royalite gas was calculated by Lewis' Rule (21) using the fugacity data for the individual hydrocarbons given in Table 2. The fugacities of the individuals were obtained by multiplying the fugacity of each component at the total pressure of the mixture (Table 2) by the mol. fraction of that component. The sum of their individual fugacities is given in Table 3 for comparison with the measured value. The discrepancy is roughly constant at one atmosphere indicating that the rule has considerable merit.

TABLE 4

PRESSURE-VOLUME DATA BELOW 1 ATMOSPHERE *

P. cm. Hg.	PV/gm.
0	95.22 (PoVo)
15	95.14
20	95.12
25	95.09
30	95.07
35	95.04
40	95.02
45	95.00
50	94.97
55	94.94
60	94.92
65	94.90
70	94.87
76	94.84

* Incorrect.

It was also considered advisable to determine the deviation of the natural gas from ideality below one atmosphere. In this work, measurements of gas volumes were made at pressures considerably below 76 cm. of mercury very frequently, and then converted to volumes at 76 cm. of mercury. The accuracy of these measurements was such as to be within the magnitude of the deviations from ideality of Royalite gas at 1 atmosphere.

The procedure was to fill one of the calibrated bulbs (Figure 9) with gas and determine its pressure and temperature. The gas was then expanded into another bulb of known volume, and pressure and temperature readings taken. This was repeated a third time and in some cases a fourth expansion was made.

The density of the gas at 60 cm. of mercury pressure and 25° C. was measured many times and a precise average value determined. The experimental conditions were only actually close enough to these chosen values so that the deviations from ideality could be neglected in calculating density at 25° C. and 60 cm. of mercury. From this density PV per gram at 25° C. and 60 cm. of mercury was obtained and all other PV products referred to one gram. A large number of expansions were carried out and the PV product per gram plotted against pressure. The best straight line was drawn and used to give the deviation factor defined by: -

$$y = (P_oV_o/PV) - 1$$

where P_oV_o is the product obtained on extrapolation to zero pressure and PV is the product at a pressure P. The residual volume "a", calculated as described previously, and related to the deviation factor as follows: -

$$y = a/V$$

was also determined in the pressure range below 76 cm. of mercury. The value of "y" and "a" at 76 cm. of mercury pressure were found to be 0~~.00040~~ .004 and 0~~.00055~~ .0053 respectively, and varied linearly with pressure to within the limit of experimental error.

X

From the P-V curves for pressures above one atmosphere the deviation from ideality is clearly indicated as increasing with increasing pressure and decreasing temperature. This is to be expected from the results of previous work on similar gases.

The relative experimental error is much greater below 25 atmospheres and hence the points obtained showed some variation. Sufficient data were obtained at these pressures to establish the position of the curve in this region and it is thought that the values presented give a true picture of the conditions. The value for one atmosphere on the 60° C. curve may be considered exact within the limits of experimental error as it was obtained

March/41 Calibrations of volume in error

— & no expansion in error — →

y [illegible] be .002 & a=.002

by density determinations at 60° C. and 76 cm. of mercury pressure.

The graph of the residual volume as a function of pressure shows "a" as a constant from 1 atmosphere to 25 atmospheres. The experimental points in this region showed wide deviations on both sides of the curve and lay in such positions that it was decided to draw the graph in the manner shown. From a consideration of Van der Waal's equation in the form

$$V = \frac{RT}{P} + b - \frac{a}{PV} + \frac{ab}{PV^2}$$

as P approaches zero, the residual volume approaches a finite value equal to b. As the pressure increases, the value of "a" increases and can become equal to and greater than "b". The curve then passes through zero and the residual volume becomes negative. This is clearly indicated from the trend of the curve in Figure 15.

Several explanations can be advanced for the fairly constant difference obtained between the experimental values of the fugacity and those calculated from the fugacity rule. The method of getting the fugacities of the individual gases is subject to error in that they are obtained by interpolation. As the curve for fugacity as a function of temperature for any one pressure is not regular, errors of one atmosphere or more might result in

the interpolated data. This would account for a portion of the difference - the rest could be classified as experimental error. The actual deviation is not very great for the higher pressures but becomes significant at lower pressures. On the whole, it may be said that Lewis' fugacity rule gives reasonably good results in so far as it has been investigated in this work.

TABLE OF SYMBOLS

V_r - Volume of Royalite gas added at 1 atmos and 25° C.
m_r - Mass of Royalite gas added.
d_r - Density of Royalite gas.
V_n - Volume of Royalite Naphtha added.
m_n - Mass of Royalite Naphtha added.
r_n - Refractive index of Royalite Naphtha.
M_n - Mean molecular weight of Royalite Naphtha.
d_n - Density of Royalite Naphtha.
m_l - Weight of liquid condensate.
V_l - Volume of liquid condensate.
V_g - Volume of gas at 1 atmos and 25° C.
d_g - Density of gas at 1 atmos and 25° C.
V^5 - Volume of C_5H_{12} in liquid condensate.
$V^5\%$ - Volume percent C_5H_{12} in liquid condensate.
r_c - Refractive index of liquid condensate.
d_r - Density residue from fractionation.
M_r - Average molecular weight from fractionation.
m_t - Total mass of liquid and gas added.
m_g - Mass of gas in phase.
w_p - Phase weight.
d_p - Phase density.
V_p - Phase specific volume.

(Superscripts L and G refer to liquid and gas phase respectively)

m_{6+} - Mass of hexanes and heavier.

M - Mol fraction - subscript below.

w - Weight fraction - subscript below.

(Subscripts N, 1, 2, 3, 4, 5 and 6+ refer to nitrogen, methane, ethane, propane, butane, pentane and hexane plus.)

G - Gas-liquid ratio added = V_r/m_n

G_1 - Gas-liquid ratio added — ccm. butanes and lighter, per gr. pentanes and heavier.

V_G - Gas phase volume at equilibrium.

G_2 - Gas phase, liquid phase volume ratios in system - V_G/V_L.

V_L - Liquid phase volume at equilibrium.

m^o_G - Weight of gas in system.

m^o_L - Weight of liquid in system.

G_L - Gas liquid ratio within liquid phase in mols butane and lighter to moles. pentanes and heavier.

G_G - Gas-liquid ratio within gas phase in mols butane and lighter to mols. pentanes and heavier.

K - Equilibrium constant - mols in gas phase to mols in liquid phase.

(Subscripts have same meaning; i.e., methane, ethane, etc.)

G^L_G and G^G_G - Mol fractions of methane to butanes in liquid phase and gas phases respectively.

G^L_L and G^G_L - mol fractions of pentanes and heavier liquids in liquid and gas phases respectively.

TABLE 5

General Experimental Data							Liquid Phase											Gas Phase		
Run No.	Temp. °C	Pressure, Abs. p.s.i.	Pressure, Abs. atmos.	V_r	m_r	m_n	m_l	V_l	r_c	V^5	$V^5\%$	d_r	M_r	V_g	d_g	m_{6+}	m_1	V_g	d_g
19	25	314.6	21.41	4129.1	3.3168	29.80	10.46	15.0	1.3947	2.68	1.785	.7238	98.7	537.3	1.150	8.78	0.02	248.1	.7346
20				4126.9	3.3148	29.91	10.50	15.0	1.3951	2.14	1.357	.7228	97.0	552.7	1.175	9.16	0.01	248.8	.7514
17	25	513.6	34.95	6978.1	5.5981	29.94	10.11	14.4	1.3938	2.15	1.493	-	98.0	830.1	1.056	8.76	0.04	419.2	.7283
18				6951.5	5.5756	29.92	10.41	15.0	1.3920	2.39	1.595	-	98.0	834.7	1.042	8.91	0.04	419.2	.7245
27				6939.9	5.5670	29.85	9.91	14.1	1.3975	1.68	1.194	.7216	98.9	853.0	1.105	8.85	0.0	418.2	.7240
12	25	713.6	48.56	9920.7	7.9587	29.45	9.81	14.0	1.3963	2.33	1.67	-	98.0	956.3	.9015	-	-	597.7	.7177
15				9931.0	7.9672	29.37	9.49	13.6	1.3954	1.96	1.44	-	98.0	1109.4	1.007	8.26	-	-	-
16				9933.5	7.9682	30.09	9.53	13.7	1.3959	2.00	1.46	-	98.0	1122.7	1.024	8.28	0.03	599.4	.7246
21	25	1013.6	68.97	14808	11.889	29.95	8.75	12.6	1.3947	1.88	1.49	.7226	97.2	1560.8	.9774	7.57	0.07	890.8	.7269
23				14766	11.854	30.00	8.60	12.2	1.3978	1.77	1.45	.7219	98.0	1567.7	.9872	7.49	0.05	899.5	.7325
24	25	1313.6	89.38	19855	16.006	29.90	7.86	11.1	1.3960	1.74	1.57	.7230	98.0	2013.1	.9402	6.77	0.07	1216.8	.7272
26				19826	15.984	30.03	7.91	11.2	1.3950	1.57	1.40	.7230	98.0	1985.2	.9457	6.93	0.07	1215.0	.7253

Royalite Naphtha

M_n - 93.7

d_n - 0.7009

r_n - 1.3955

Royalite Gas

N_N - 0.0500

N_1 - 0.7957

N_2 - 0.0947

N_3 - 0.0403

N_4 - 0.0156

N_5 - 0.0037

TABLE 6

Gas Analysis

Run No.	Volume % Liquid Phase Gas							Volume % Gas Phase Gas						
	CH_4+N_2	N_2	CH_4	C_2H_6	C_3H_8	C_4H_{10}	C_5H_{12}	CH_4+N_2	N_2	CH_4	C_2H_6	C_3H_8	C_4H_{10}	C_5H_{12}
19	55.62	-	-	17.35	15.21	11.18	0.64	92.61	5.75y	86.86y	4.94	1.33	1.01	0.11
	55.85	-	-	17.02	14.96	11.53	0.64							
20	54.60	-	-	16.69	15.25	12.98	0.48	92.79	5.75	87.04	4.62	1.33	1.11	0.15
	54.67	3.45	49.22	16.77	14.96	12.97	0.63							
17	62.31	-	-	17.39	12.55	7.21	0.54	92.84	-	-	6.07	0.33	0.62	0.14
	62.26	3.50y	58.76y	17.39	12.60	7.20	0.55	92.63	5.80y	86.83y	6.87	0.18	0.17	0.15
18	62.40	-	-	17.93	12.64	6.13	0.90	92.97	-	-	5.04	1.39	0.48	0.12
	62.40	3.50y	58.90y	17.90	12.76	6.05	0.89	93.00	5.86y	87.14y	5.09	1.31	0.48	0.12
27	58.90	-	-	17.14	12.38	10.78	0.80	92.77	5.86y	86.91y	5.11	1.28	0.71	0.13
	58.95	3.50	55.45	17.14	12.66	10.46	0.79							
12	71.93	-	-	18.62	6.09	1.62	1.74	93.20	-	-	5.22	1.21	0.25	0.12
	72.20	-	-	18.71	6.14	1.51	1.44	93.25	5.70y	87.55y	5.19	1.21	0.24	0.11
15	65.11			17.70	11.60	5.49	0.10	-	-	-	-	-	-	-
	65.09	3.40y	61.69y	17.71	11.96	5.14	0.10							
16	64.72	-	-	17.66	11.81	5.71	0.10	92.86	-	-	5.35	1.28	0.38	0.13
	64.71	3.40y	61.31y	17.67	11.82	5.71	0.09	92.87	5.70y	87.17y	5.93	0.62	0.42	0.16
21	67.58	3.04	64.54	16.92	11.11	2.49	1.90	92.71	5.75y	86.96y	5.52	1.42	0.22	0.13
	67.69	-	-	16.88	10.98	3.82	0.63	92.67	-	-	5.52	1.45	0.24	0.12
23	67.12	-	-	16.63	10.38	5.00	0.87	93.30	-	-	4.86	1.25	0.45	0.14
	67.19	3.80	63.39	16.60	10.50	4.80	0.91	93.29	5.75	87.54	4.86	1.28	0.45	0.11
24	70.06	2.30	67.76	15.90	9.58	4.14	0.32	92.08	5.70	86.38	5.77	1.56	0.48	0.11
	70.17	-	-	15.72	9.63	4.15	0.33	92.03	5.50	87.03	5.71	1.52	0.64	0.10
26	70.98	2.50	68.48	15.93	7.66	3.49	1.94	92.35	6.20	86.15	5.64	1.57	0.32	0.12

y Extrapolated values

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TABLE 7

General Derived Data, at 25°C.

Run No.	19	20	17	18	27	12	15	16	21	23	24	26
Press., p.s.i.	314.6	314.6	513.6	513.6	513.6	713.6	713.6	713.6	1013.6	1013.6	1313.6	1313.6
atmos.	21.41	21.41	34.95	34.95	34.95	48.56	48.56	48.56	68.97	68.97	89.38	89.38
W_p^L	11.08	11.15	10.99	11.28	10.85	-	10.61	10.68	10.28	10.15	9.753	9.787
d_p^L	0.6681	0.6723	0.6626	0.6801	0.6541	-	0.6397	0.6440	0.6198	0.6120	0.5881	0.5901
V_p^L	1.497	1.487	1.509	1.470	1.529	-	1.563	1.553	1.613	1.634	1.700	1.695
m_g^L	0.6180	0.6495	0.8769	0.8693	0.9427	-	1.118	1.149	1.526	1.548	1.893	1.877
V_n	42.52	42.67	42.72	42.69	42.59	-	41.90	42.93	42.72	42.80	42.66	42.84
m_g^G	0.182	0.187	0.305	0.304	0.3028	-	-	0.434	0.648	0.660	0.885	0.881
W_p^G	0.202	0.197	0.345	0.344	0.3028	0.459	-	0.464	0.718	0.709	0.955	0.951
d_p^G	.01803	.01758	.03079	.03070	.02702	-	-	.04141	.06407	.06326	.08521	.08488
V_p^G	55.46	5688	32.48	32.57	37.01	-	-	24.15	15.16	15.81	11.74	11.78
G_g^L	.1626	.1657	.2377	.2319	.2488	-	.3087	.3102	.3986	.4023	.4926	.4809
G_L^L	.8374	.8343	.7623	.7681	.7512	-	.6913	.6898	.6014	.5927	.5074	.5191
G_L	.1942	.1986	.3118	.3019	.3312	-	.4465	.4497	.6628	.6872	.9708	.9264
G_g^G	.9723	.9850	.9672	.9675	.9987	.9821	-	.9819	.9728	.9803	.9798	.9796
G_L^G	.0277	.0150	.0328	.0325	.0013	.0179	-	.0181	.0272	.0197	.0202	.0204
G_G	35.10	65.67	29.49	29.77	768.2	54.86	-	54.25	35.76	49.76	48.50	48.02
V_G	132.0	132.0	130.4	131.7	129.2	-	-	127.1	123.2	122.2	116.8	116.8
G_2	2.869	2.873	2.741	2.864	2.647	-	-	2.495	2.251	2.192	1.912	1.910
m_G^o	2.380	2.321	4.016	5.362	3.490	-	-	5.262	7.896	7.733	9.958	9.916
m_L^o	30.74	30.90	31.52	31.45	31.93	-	-	32.80	33.94	34.12	35.95	36.09
G	138.6	138.0	233.1	232.3	232.5	-	338.1	330.1	294.5	292.2	664.0	660.3
G_1	137.9	137.3	231.7	230.9	231.1	-	335.7	327.8	490.0	487.7	656.7	653.1
m_T	33.12	33.22	35.54	35.50	35.42	-	37.34	38.06	41.83	41.85	45.91	46.01
V_L	46.01	45.96	47.57	46.25	48.81	-	-	50.93	54.76	55.75	61.13	61.16

TABLE 8

		Liquid Phase Weight Fractions							Liquid Phase Mol Fractions						
Run No.	P.atmos	w_1^L	w_N^L	w_2^L	w_3^L	w_4^L	w_5^L	w_6^L	N_1^L	N_N^L	N_2^L	N_3^L	N_4^L	N_5^L	N_6^L
19	21.41	.01658	.00192	.01026	.01320	.01310	.1521	.7924	.08557	.00565	.02812	.02469	.01859	.1745	.6629
20		.01660	.00196	.01017	.01347	.01523	.1208	.8215	.0852	.0058	.0279	.0252	.0216	.1380	.6964
17	34.95	.02904	.00303	.01611	.01708	.01291	.1235	.7972	.1404	.00836	.04155	.03004	.01073	.1327	.6296
18		.02851	.00296	.01626	.01690	.01068	.1345	.7902	.1378	.00819	.04192	.02971	.01424	.1444	.6238
27		.02850	.00315	.01653	.01770	.01965	.09889	.8155	.1391	.00878	.04301	.03143	.02645	.1072	.6441
15	48.56	.04219	.00407	.02270	.02216	.01317	.1158	.7789	.1907	.0105	.0547	.0364	.0164	.1164	.5749
16		.04220	.00410	.02280	.02230	.01420	.1174	.7760	.1903	.0106	.0549	.0367	.0177	.1178	.5720
21	68.97	.06414	.00528	.03146	.03016	.01136	.1200	.7365	.2608	.0123	.0682	.0446	.0127	.1085	.4929
23		.06400	.00672	.03147	.02900	.01794	.1133	.7379	.2604	.0156	.06827	.0429	.02014	.1024	.4904
24	89.39	.09155	.00544	.03999	.03563	.02027	.1134	.6943	.3351	.0114	.07813	.0475	.02048	.09234	.4151
26		.0907	.0058	.0396	.0279	.0167	.1116	.7078	.3358	.0123	.0781	.0376	.0171	.0917	.4271

TABLE 9

Gas Phase

Run No.	Pressure Atmos.	Weight Fractions w_1^G	w_N^G	w_2^G	w_3^G	w_4^G	w_5^G	Mol Fractions N_1^G	N_N^G	N_2^G	N_3^G	N_4^G	N_5^G
19	21.41	.6875	.0800	.0731	.0288	.0292	.1014	.8455	.0560	.0480	.0129	.0099	.0277
20		.7237	.0838	.0720	.0301	.0337	.0567	.8586	.0567	.0456	.0131	.0110	.0149
17	34.95	.6869	.0801	.0959	.0055	.0112	.1204	.8421	.0562	.0627	.0024	.0038	.0328
18		.6843	.0796	.0744	.0292	.0137	.1188	.8445	.0562	.0491	.0131	.0046	.0325
27		.7662	.0906	.0845	.0309	.0226	.0052	.8691	.0586	.0511	.0128	.0071	.0013
12	48.56	.7315	.0834	.0814	.0278	.0075	.0684	.8606	.0561	.0511	.0119	.0024	.0179
16		.7257	.0824	.0883	.0219	.0211	.0690	.8571	.0560	.0556	.0093	.0039	.0181
21	68.97	.6971	.0808	.0830	.0316	.0067	.1008	.8468	.0560	.0538	.0140	.0022	.0272
23		.7243	.0832	.0753	.0288	.0135	.0749	.8594	.0564	.0477	.0124	.0044	.0197
24	89.38	.7035	.0800	.0879	.0346	.0166	.0756	.8480	.0549	.0563	.0151	.0055	.0202
26		.7039	.0885	.0865	.0353	.0095	.0763	.8450	.0608	.0553	.0154	.0031	.0204

TABLE 10

Equilibrium Constants

Pressure lbs/sq.in.	Atmos.	K_1	K_2	K_3	K_4	K_5
314.6	21.41	9.937	1.6710	.5116	.5365	.1680
513.6	34.95	6.152	1.1860	.4038	.2135	.2158
713.6	48.56	4.465	.9406	.3378	.1719	.2271
1013.6	68.97	3.227	.7870	.3126	.1875	.2253
1313.6	89.38	2.519	.7148	.3214	.2368	.2102

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The Two-Phase, Royalite Gas-Naphtha System

The direct experimental data are presented in Table 5, the derived data and intensive properties being given in Tables 6, 7, 8, 9 and 10. This material will be discussed as to precision and significance.

Experimental conditions at all times were carefully controlled. Temperatures were read on thermometers calibrated against a Bureau of Standards thermometer. Oil baths, where used, were maintained at ±0.15° C. of the desired temperature.

The pressure of the gas added to the solubility system was measured by means of the dead weight piston gage, and was accurate to within less than one pound of the desired pressure. This introduces a relative error at low pressures of possibly 0.5%, but at high pressures it becomes negligible.

The volume of the gas added, V_r, was determined by the weight of mercury used to displace the added gas. This was weighed to 0.1 gram and on the mass of mercury used (approximately 2800 g), the error is negligible.

Knowing the volume of gas added, its temperature, pressure, and density from P-V data, the mass added was readily calculated as $m_r = V_r d_p$. The accuracy of the mass is determined largely by the accuracy of the density determinations. This has been discussed under P-V data.

The mass of naphtha, m_n, was determined by weighing the liquid sample burette plus liquid before and after discharging. Some slight loss may occur at the time of transfer of the naphtha to the solubility pipettes due to improper drainage of the stem of the burette. This cannot be determined quantitatively, but every precaution was taken to avoid such loss.

The volume of the liquid condensate was read from the graduated condenser in which the material was caught. The error in this reading might be as large as 1% but this is not serious since the only determination based on this volume is the volume percent of pentane, the weight of the condensate, m_1, being used for all other purposes.

The refractive index, r_c, of the condensate was determined using a Pulfrich refractometer. Due to the volatility of the condensate the refractive index must be determined without delay after the condenser has been opened.

After fractionation to remove the pentane, the refractive index, density and mean molecular weight of the residue was determined. This has been fully discussed in Appendix II.

The volume percent of pentanes, $V^5\%$, introduced a larger error than was desirable in this work. The

volume of pentanes was small (about 2 c.c.) and was read to within ±0.05 c.c., thus introducing a possible error as great as 5%. This shows up as a large error only in derived data for pentanes, and appears as a much smaller error in the relatively larger mass of the remaining materials. It is doubtful that any better data on pentanes can be obtained. The volume percent is read probably as accurately as the method of analysis, fractional distillation, warrants.

Forced circulation of air in the cabinet enclosing the calibrated measuring bulbs maintained a uniform temperature of the bulbs while gas volumes were being measured. Temperature within the cabinet was read as closely as possible to 0.01° C. by means of a long scale calibrated thermometer. The pressure of the gas was determined by means of the precision manometer. The absolute error in reading the manometer is ±0.01 cm. but the relative errors vary according to the pressure of the gas being measured, and are insignificant except in connection with gas analysis described later. All volumes of gas from the solubility pipettes were reduced by the ideal gas laws at 25° C. and 76 cm. of mercury pressure.

Duplicate density determinations were made on this gas by weighing a calibrated bulb containing the gas at known pressure and temperature. Stop cock grease was

removed, the bulb wiped carefully and hung in the balance for fifteen or twenty minutes before weighing. The evacuated bulb was weighed frequently. The density was expressed as grams per liter at 25° C. and 76 cm. of mercury pressure. Determinate errors in the density determinations were negligible, and utmost precautions were taken to keep indeterminate and personal errors at a minimum.

Very little liquid condensate was obtained from the gas phase pipette, consequently a larger error was introduced into gas phase calculations. The liquid obtained was considered to be pentanes and varied from zero to 0.07 gram over the range of pressures studied. Weighings were made to only 0.01 gram. This gas phase condensate introduces the largest error that occurs in this work, and a more suitable method for determining the mass of the condensate will be used in future. The division of the contents of a phase sampling pipette into gas and liquid as shown in Table 5 is somewhat arbitrary. Precise separation between the pentanes and butanes is desirable, but not essential. It is essential, however, that the butanes be entirely removed from the liquid condensate. To ensure this, distillation from the condenser train was continued until some pentanes were removed as well as all the butanes. No particular efforts were made to reproduce this separation.

The data in Table 6 are the result of gas analyses by the low temperature-low pressure apparatus, and combustion to determine nitrogen. These analyses were run in duplicate on every gas fraction obtained from both the upper and lower pipettes in the solubility work. These volumes percent are obtained from the volume of each component as a percentage of the sum total of gas recovered from the column. This gives, as pointed out in Appendix I, within the limits of experimental error, the correct molecular composition of the gas.

From the gas analysis, the mol number of each component was calculated, and from the mol numbers were calculated the mol fractions N_1^L, N_2^L, etc. (Table 8 and Figure 17) for gas out of the liquid phase pipette, and N_1^G, N_2^G etc. (Table 9 and Figure 18) for the gas from the gas phase pipette. Knowing the total weight of each phase w_p^L and w_p^G (Table 7), the weight fractions corresponding to the mol fractions were also calculated. Weight of hexane and heavier components was found by difference, and the weight fractions calculated from this. Mol fractions were calculated from the experimentally determined mean molecular weight of fractionation residues containing the hexane and heavier components, and the mass of this material as determined by difference.

Some relatively large differences occur in these quantities between runs, especially in the material from

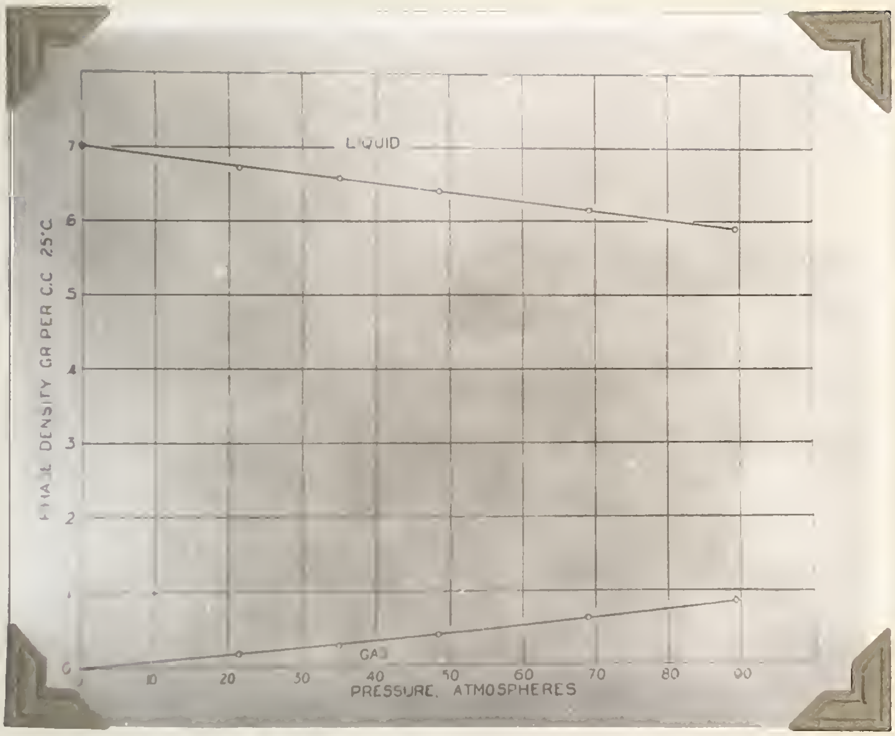


FIGURE 16: Phase Density-Pressure Relationship.

the gas phase pipette. This is due to the small amount of liquid condensate (pentanes) obtained and consequent large errors because the liquid forms a relatively large portion of the total mass of material in the pipette. In the liquid phase pipette, the pentanes form a much smaller percentage of the total mass, and the relative errors introduced are correspondingly smaller.

The phase densities (Table 7) were determined from the total mass of material in each pipette and the known volumes of the pipettes. This was expressed in grams per cubic centimeter and is shown graphically in Fig. 16. As might be expected, there was some slight irregularity at low pressures possibly due to slight differences in pressure and temperature, the effect of which on the solubility produces relatively larger errors at these lower pressures. As the pressure was increased the density of the gas phase increased, and at the pressures used, this increase was practically linear. This increase in density with pressure was the result of the action of three factors. First, the natural increase in density with pressure; second, a decrease in density of the gas due to the preferential solution in the liquid of the ethane, propane and butane; and third, an increase due to the transfer of pentanes and other volatile liquids

as vapour to the gas phase. Comparing the gas phase density with the density of the Royalite gas at equal pressures, it will be seen that the Royalite gas has the greater density. For example, at 80 atmospheres, the density of Royalite gas is 0.080 gram per cubic centimeter and the phase density is 0.075 gram per cubic centimeter. Evidently in the pressure range investigated, the solution of the heavier hydrocarbons in the gas by the liquid produces a greater mass transfer than the vaporization of liquids into the gas phase. The course of the curves in Figure 18 suggests that at pressures not far above 80 atmospheres, the gas phase will exceed in density Royalite gas. The work on mean molecular weights (Appendix II) showed that no measurable transfer of hexane or heavier hydrocarbons from the liquid phase to the gas phase took place within this pressure range. The density of the liquid phase decreased almost linearly with increased pressure, and this behavior may be attributed to the transfer of pentanes to the gas phase and the increased solubility of gas in the liquid phase.

The gas-liquid ratios in the phases G_L and G_G were calculated from the mol fractions and the results are shown graphically in Figure 19. As can be seen from the graph, little transfer of material took place until a pressure of about 65 atmospheres was reached. The gas-liquid ratio of the gas phase then began to change rapidly

due to transfer of pentanes. By analogy to previous work(18), it was expected that the solubility of gas in the liquid; i.e., G_L, would increase more rapidly than the pressure. This effect is barely noticeable in the pressure range used and will become more pronounced at higher pressures. The effect is attributable to the change in properties of the liquid, approaching those of the gas phase, due to increasing content of dissolved gas.

Knowing the total volume of the solubility apparatus, it was possible to calculate the phase volumes in the apparatus. These have been listed in Table 7 under V_L for the liquid phase and V_G for the gas phase. The ratio V_G/V_L has been listed under G_2. As the pressure increased the ratio of gas to liquid decreased steadily. This was to be expected from the regular change in phase density, Figure 16, and was due to the solution of gas in the liquid increasing the liquid phase volume as the pressure increased. A slightly larger decrease took place between 69 and 89 atmospheres and would be expected to accelerate due to the increasingly great transfer of liquid components to the gas phase. The behavior of this ratio, G_2, will depend, for any particular pair of starting materials, on the initial amount of liquid taken. The ratio may decrease as in the present case, or increase if much less original naphtha had been used. The system

may become single phase through the disappearance of either one of the phases. There is, however, a unique condition for which G_2 varies only slowly, if at all, and the system becomes single phase through approach to identity of both phases. These effects will only be demonstrated by further work on the present system but have been shown with other simpler systems(18).

The ratio of the gas-liquid added to the solubility apparatus has been shown in Table 7 under G. This ratio is the volume of Royalite gas in cubic centimeters divided by the mass of naphtha in grams. A more characteristic ratio is given under G_1. This gives the ratio of butanes and lighter gases to pentanes and heavier liquids as determined by analysis of the original materials. Here the ratio increased steadily as the pressure increased, due to the addition of larger amounts of gas. In a system containing always the same amount of liquid and gas the ratio would remain constant over the range in which the present system shows a uniformly changing ratio. Towards the upper limit of the pressure range the ratio increased more rapidly than the pressure and would be expected to continue doing so until a single phase is reached. This is explicable on the change in gas solubility in the liquid, discussed previously.

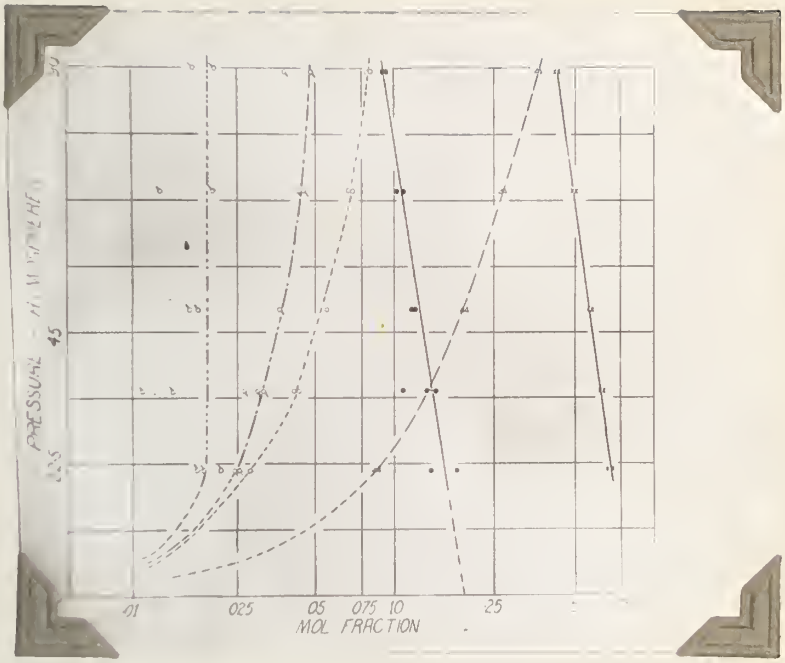


FIGURE 17: Mol Fraction-Pressure Relationship for the Liquid Phase.

Legend

Methane — —Δ— —Δ Butane ♂···—···—♂

Ethane ○— —○— — Pentane ——●——●

Propane ○·—○— - — Hexane ——X——X

In Table 8 is given the mol fractions for the liquid phase. These data are shown graphically in Fig. 17. Increased pressure produced increased solubility of methane, ethane and propane in the liquid. The solubility of these gases shows signs of approaching a limiting equilibrium value at the highest pressure used. Over the pressure range used, butane showed no change in solubility within the limit of error. In this case, because of the small amount of butane in the system, the relative errors are large. By comparison with the behavior of the other gases, however, it is probable that the solubility of butane has reached the equilibrium value and is independent of pressure below 89 atmospheres. The curves have been extended below the pressures examined to indicate their probable courses in that region. The mol fractions of liquid material check quite well, especially the hexane and heavier fraction. This must be expected as it constitutes a large percentage of the total mass. The decrease in mol fraction of hexane and heavier, results from the increased solubility of gases in the liquid phase with increase in pressure, since mean molecular weight determinations on this fraction showed no measurable transfer of hexane to the gas phase. The mol fraction of pentane also decreased with increased pressure, but here two effects are apparent. Transfer of

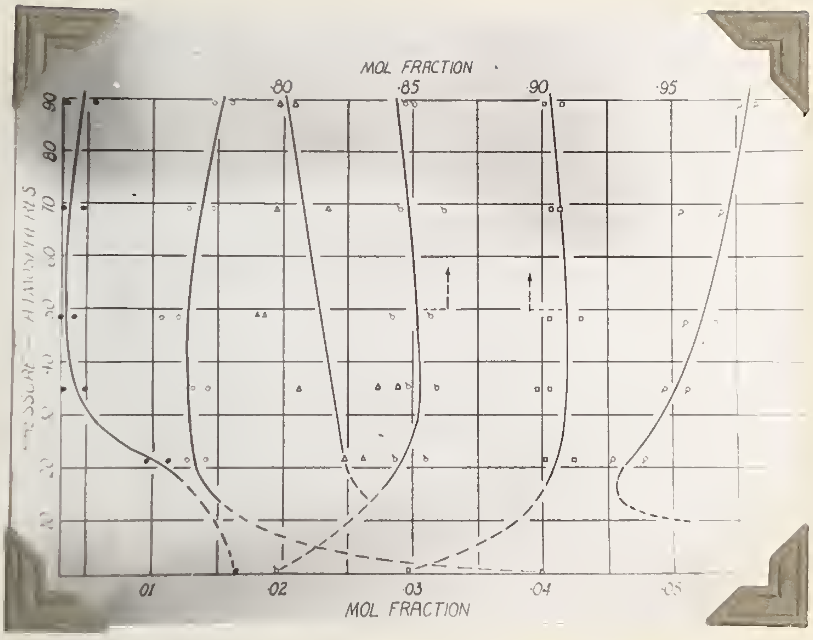


FIGURE 18: Mol Fraction-Pressure Relationship for the Gas Phase.

Legend

Methane	——ɓ——ɓ	Butane	——●——●
Ethane	ϙ——ϙ——	Pentane+	——△——△
Propane	—— ○ ——○	Methane+N_2	——□——□

pentane to the gas phase decreased the mol fraction, while at the same time increased solubility of gases also decreased it.

The mol fractions of the gas phase are listed in Table 9 and shown graphically in Figure 18. These show more irregularity than in the case of the liquid phase because of the method for determining the liquid condensate from the gas phase. This condensate varied in weight from zero to 0.07 gram and was weighed to only ±.005 gram. A small variation in the weight of this material, considered pentanes, noticeably affected the mol fractions of the other components, and greatly affected the mol fraction of pentanes. For this reason, not even the general trend of the pentane curve could be determined. The values determining its position on the graph were obtained by deducting from one the sum of the graphical values for all the other components. This gives a curve such as would be expected from considerations developed previously(18). The position of the other curves in Figure 18 is also somewhat uncertain, particularly in the case of methane and methane plus nitrogen. These latter curves might well be parallel to the pressure axis and the course given them is only probable. The mol fraction of pentane decreases with increased pressure because the transfer of pentane from the liquid phase was not sufficiently great to counter-

cally in Figure 20. As can be seen from the graph there is a rapid decrease in the equilibrium constants, except K_5, as the pressure was increased. This is due to the preferential solution of these components in the liquid phase as the pressure was increased. The rate of decrease, however, diminishes with increasing pressure, and in the case of propane and butane a definite trend to higher values is seen. At still higher pressures, as yet unexamined, the equilibrium constants will all approach the value one, becoming one when the system is single phase. Comparison of Figures 17 and 18 show that this is the trend of all the curves. For pentane in the gas-naphtha equilibrium system at one atmosphere, the value will probably be fairly large due to the high vapor pressure of pentane and the large percentage of pentane present. The equilibrium constant would decrease rapidly with increasing pressure in the region 1 to 23 atmospheres, and suggests that the trend of the K_5 curve at low pressures should be in the opposite direction to that shown. The position of the K_5 line is very uncertain because of the errors involved in the determination of N_5 in the gas phase discussed previously. A consideration of the pentane curves in Figures 17 and 18 suggests that K_5 should reach a minimum at some pressure above those studied, and after that should increase to the value of one when a two phase system of identical phases is reached.

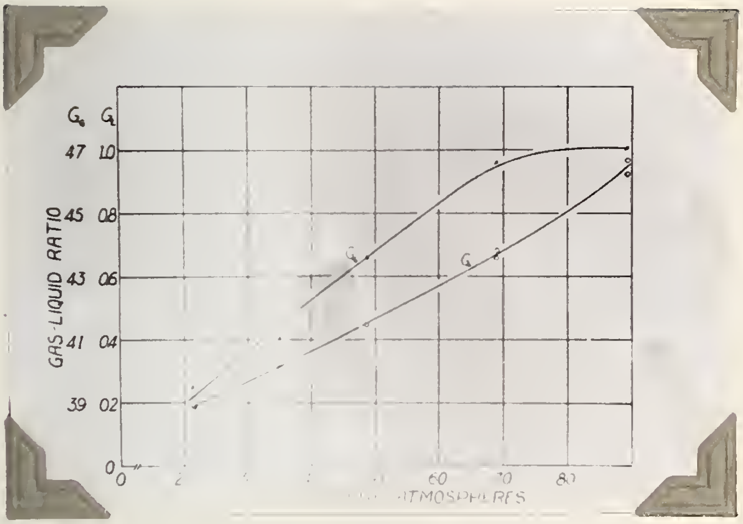


FIGURE 19: The Variation of the Gas-Liquid Ratio in the Phases with Pressure.

act the diluting action of increased amounts of gas added with increasing pressure. Ultimately, however, with sufficiently high pressures, the pentane content may be expected to pass through a minimum and increase.

The course of the curves for ethane, propane and butane is explicable on the basis of the change in properties of the liquid phase. With increasing pressure the gases dissolve in relative amounts determined by their concentration in the gas. The gas is principally methane and it dissolves to a much greater extent than the others. As the pressure increases, the liquid phase becomes more like the gas phase and transfer of components heavier than methane to the gas phase becomes appreciable and ultimately, in this case at 30 to 50 atmospheres, the ethane, propane and butane content of the gas begins to increase. Presumably, as the course of the curves in Figures 17 and 18 suggest, the concentrations of the gases in both phases will reach the same value and the system become a single phase.

The distribution of each component between the two phases is listed in Table 10 as equilibrium constants K_1 - K_5. These constants represent the ratio of mol fraction in the gas phase to mol fraction in the liquid phase at the pressures studied. They are shown graphi-

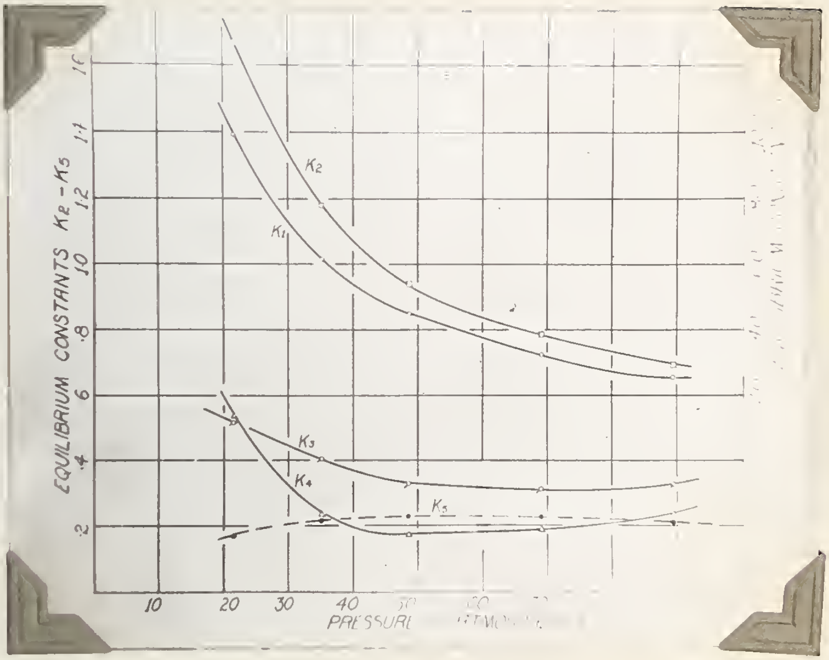


FIGURE 20: Equilibrium Constants as Functions of Pressure.

Legend

Methane - K_1	Butane - K_4
Ethane - K_2	Pentane - K_5
Propane - K_3	

Data as a whole in this preliminary investigation of complex systems are behaving as might be predicted in the light of previous work on simpler systems (5, 6, 7 and 8). The vapor pressure of pentane increases with increasing pressure as is predicted by Poynting's Rule and shown in the simple systems. The behavior of the gases ethane, propane and butane is more complex, since initially there is none in the liquid, solution takes place at low pressures. As the pressure rises, the vapor pressure of these gases in the solution begins to increase - just as for the pentanes, etc. - and the amount of corresponding components in each phase approaches equality at some high pressure. No attempt has been made to correlate the results with theory. It appears highly improbable that analytical expressions can be developed for such systems as these. The systems are made of a large number of components and consequently the variables are too numerous for mathematical expression of the conditions of equilibrium in terms of all components. It is probable that further work will bring to light impirical rules relating the gas phase composition in terms of individual components, and some such property of the original liquid phase as its molecular weight.

Interpretation of the results in their relation to Turner Valley may be somewhat premature. Originally

pressures in the naphtha producing formation in the Valley were around 2000 - 2500 pounds per square inch and the gas-oil ratio was about 1000 - 2000 cubic feet per gallon. At the highest pressure used here, 1300 pounds per square inch, the gas-oil ratio in the same units is approximately 1500 cubic feet per gallon, and would presumably be much less at 2000 - 2500 pounds per square inch. From another point of view, when the average Valley pressure had dropped to 1300 pounds per square inch, the gas-oil ratio was roughly, over the field, 3000 cubic feet per gallon. It must be pointed out, however, that equilibrium between naphtha and gas probably would not be maintained. If these estimates are not in error by more than 30%, it appears that there was no liquid phase in the naphtha producing formation in the earlier part of the field's life.

SUMMARY

The pressure volume behavior of Royalite gas has been studied at two temperatures, 25° C. and 60° C., over a pressure range from 15 cm. of mercury to 2500 pounds per square inch. Residual volumes and fugacities for this gas were calculated from experimental data and compared with fugacity values calculated by Lewis' fugacity rule.

Changes in existing apparatus, to enable known amounts of liquid and gas to be added, and to overcome certain defects, have been described.

Solubility equilibria between the complex mixtures occurring in Royalite gas and Royalite naphtha have been investigated at 25° C. over a range of pressures from 23 to 89 atmospheres. Detailed, precise analyses of the equilibrium phases have been carried out and the acquired data used in interpreting the behavior of the complex system.

The detailed construction, calibration and operation of a new low temperature-low pressure fractionating column for gases has been described in Appendix I.

The determination of mean molecular weight, density and refractive index of certain mixtures from the main project, and the correlation of these properties has been described in Appendix II.

APPENDIX I

Low Temperature-Low Pressure Fractionation

Introduction

In connection with the determination of phase composition as described previously in this thesis it was necessary to employ some means of analysis. Principal interest is attached to the content of lighter hydrocarbons from methane through to pentane and nitrogen. In the process of removing the phase samples, a primary separation was made into a gas consisting of pentane and lighter hydrocarbons and a liquid containing pentanes and heavier hydrocarbons. It was necessary to analyse this separated gas with a precision comparable with the other measurements. Further, in view of the number of such analyses, a relatively simple, rapid and inexpensive method was desirable. In this appendix, the development and application of a new method of analysis of hydrocarbon gas mixtures by fractional distillation at low pressures will be described.

Literature Review and Theoretical Considerations

The original attempts at fractionation of complex gaseous mixtures were done by Ramsay and Travers(33). They studied the gaseous elements of the atmosphere by condensing samples of air at low temperatures and effecting separation by repeated distillations and condensations at low pressures. Burell, Seibert and Robertson(12), using a modification of Ramsay's work, developed the first apparatus and methods for the fractional distillation of natural gas. The apparatus was complicated and the procedure tedious and time-consuming. Further, slow combustion analysis had to be made to separate the binary mixtures obtained from the fractionation.

Shepherd and Porter(46) improved on Burell's methods by employing a series of condensers and pumps and repeated distillations and condensations. The methods and apparatus are an improvement on previous work in that it is somewhat shorter and separation is obtained with a high degree of accuracy.

Podbielniak(32) devised a method employing a conventional fractionating column of high efficiency working at low temperatures and at pressures from atmospheric to 100 mm. of mercury. His apparatus possesses the advantage over previous attempts in that the time is

considerably shortened for a complete analysis. The limit of accuracy is, however, reduced to that of engineering calculations.

Using the basic methods of Shepherd, Ward(49) devised an improved apparatus which cuts the analysis time to about three hours, and gives results comparable in accuracy with those of Shepherd. Ward also employs a train of condensers - five in number - which are kept accurately at certain temperatures by the use of liquid air baths and electric heaters. By varying the temperature gradient over four of the condensers and keeping the fifth at liquid air temperature, separation is effected at pressures of less than one mm. of mercury. Ward's apparatus possesses considerable advantages over previous work. It shortens the time of analysis required by Podbielniak and Shepherd, uses much less liquid air and is satisfactory with small gas samples of the order of 100 c.cm. The accuracy of the method is comparable with that obtained by Shepherd.

Von Elbe and Scott(48) have applied low temperatures and pressures to the fractionation of liquids having almost identical boiling points at atmospheric pressure. The procedure involves no reflux and consists mainly of drawing a sample of less than 0.1 c.cm. through a temperature gradient at a slow uniform rate. A separation of p-

and m- xylenes to within a few percent is reported by the authors.

The use of low temperatures and pressures and the omission of a long fractionating column, reflux, and a large sample, depends on two well known principles. At low temperatures, the vapour pressure ratios of successive members of a hydrocarbon series increase greatly and almost complete separation is possible in simple fractionating apparatus.

Table II

Vapour Pressure Ratios

Hydrocarbons	Temperature °C.					
	-175	-160	-150	-140	-120	-100
Methane-Ethane	2000	450				
Ethane-Propane		66	39			
Propane-i-Butane			16.5	5.5		
Propane-n-Butane			18.2	18.3		
n-Butane-i-Pentane					6.2	1.8
i-Butane-i-Pentane					25.0	6.3

Table II shows the ratios of the vapour pressures of successive members of the paraffin hydrocarbon series at several temperatures above that of liquid air. The

data were obtained from the International Critical Tables and extrapolated for the lower temperatures.

In addition to the increased vapour pressure ratios, the actual amount of the vapour phase over the liquid phase is small at reduced temperatures, and hence a negligible amount is left at the completion of each distillation. Further, the small volumes of liquid and gas phase and the relatively large surface of contact permit rapid establishment of equilibrium conditions.

Employing essentially the same ideas used by Ward, apparatus was devised which combines his condenser train into one fractionating column and a liquid air trap. The apparatus and methods devised possess several advantages over Ward's set up.

Materials

Prior to the fractionation of unknown samples, several synthetic mixtures were prepared in order to determine the best operating conditions for the column, and to develop a technique in using it. To make up these synthetic mixtures in somewhat the same proportions and containing the same constituents to be met with in the solubility work, it was necessary to obtain samples of methane, ethane, propane, n-butane and i-butane in as pure a state as possible.

Methane was prepared from Viking gas which in itself contains 95 % CH_4. The gas was admitted to the analytical apparatus (Figure 9) and passed through condensers B and C, 25 c.cm. of liquid being condensed. Condenser C was kept at -165° C. to -170° C. and B at liquid air temperature. Non-condensible gas was removed by repeated evacuation to a pressure of 5 cm. of mercury. The liquefied material was allowed to evaporate, the first and last thirds being discarded. The material retained was distilled and again the first and last portions were discarded, the middle third retained and transferred to a storage bulb. Density determinations were made on the stored gas and it was found to have a density of 0.7183 g/l at 0° C. and 76 cm. of mercury pressure. The density of methane as given by the I.C.T. is 0.7168 g/l at 0° C. and 76 cm. of mercury pressure. Precision combustion analysis(3) showed no higher hydrocarbons - any impurities present being traces of nitrogen.

Ethane was prepared by the Grignard reagent method. The reagent was prepared by treating Ethyl Bromide in anhydrous ether solution with magnesium wire. Crystalline iodine was added as a catalyst. The reagent was then hydrolized to give ethane. The gas produced was passed through a water condenser, a trap surrounded by ice and water, followed by a coil immersed in a freezing mixture

of ice and salt. This removed nearly all the ether carried over with the ethane. To remove the last trace of ether, the gas was bubbled slowly through fuming sulphuric acid followed by a 10% solution of KOH to remove sulphur trioxide. The gas was then passed to a small gasometer. Tests on the gas indicated that a small quantity of unsaturated hydrocarbons was present, so all the gas was passed through a saturated solution of bromine water followed by KOH solution. It was then dried by passing it over P_2O_5 and transferred to the analytical apparatus (Figure 9).

Using liquid air and repeatedly distilling the gas back and forth between condensers B and C and discarding the first and last quarters, a sample was obtained which had a density of 1.3569. This may be compared with the figure 1.3535 given by Beattie, Hadlock and Raffenbergar(1). Precision combustion analysis(3) showed a carbon-hydrogen ratio in the gas of 3.33.

Propane was obtained from a cylinder of the commercial grade 98% gas purchased from the Carbide and Carbon Chemicals Company. The gas was condensed in condenser ~~A~~ B (Figure 9) at -160° C. until a liquid sample of about 20 c.cm. was obtained. This sample was vaporized and 3 c.cm. discarded. The temperature of condenser ~~A~~ B was raised to -100° C. and condenser ~~B~~ C kept at -143° C. The Toepler pump

was operated till the pressure was 0.1 mm. of mercury. The sample was then vaporized from ~~A~~ B and condensed in condenser ~~B~~ C, portions of the gas being pumped off frequently. The temperatures of the condensers were again adjusted, and the system pumped down to 0.05 mm. of mercury for one-half hour. The sample was then vaporized and pumped to a storage bulb. Its density was found to be 2.0021 g/1 at 0° C. and 76 mm. of mercury pressure. This may be compared with the value 2.020 as given in the I.C.T.

n-Butane and i-butane approximately 99.57% pure were obtained in cylinders from the Ohio Chemical and Manufacturing Company. Approximately 25 c.cm. of each gas, as liquid, was condensed in condenser ~~A~~ B at -80° C. This sample was distilled and the first 10 and the last 5 c.cm. were discarded and the middle 10 c.cm. were vaporized and pumped to the storage bulbs after density determinations had been made, and successive readings of the vapor pressure at this temperature gave a constant value comparable with that recorded in the I.C.T. The density of n-butane was 2.6685 g/1 and i-butane 2.6467 g/1 at 0° C. and 76 cm. of mercury pressure - compared with the value of 2.673 for i-butane given by the I.C.T.

It should be pointed out that relatively few values of density for the gaseous paraffins except methane are available and agreement is poor amongst them. The

materials prepared here are believed to be of high purity because of unchanging density and vapour pressure upon distillation.

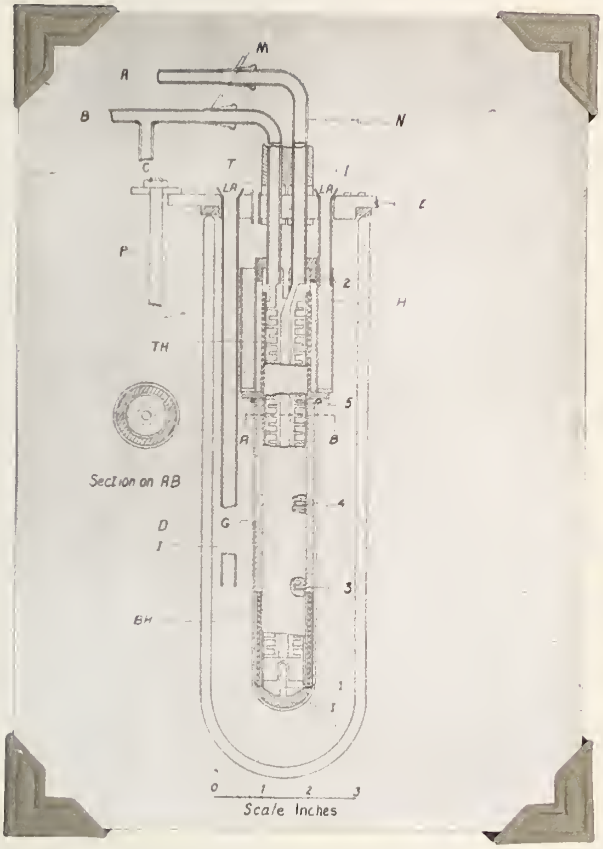


FIGURE 21: Detailed Scale Drawing of the Low Temperature-Low Pressure Fractionating Column.

Apparatus

A detailed drawing of the fractionating column is shown to scale in Figure 21 and a conventional drawing showing the associated apparatus appears in Figure 9.

Preliminary experiments(10) with a small column of glass showed that excellent heat transmission and a controlled temperature gradient from top to bottom of the column were necessary. In order to achieve these requirements, the column was made entirely of metal and of small size. Further, it was designed to be used in an inverted position; what may be called the still being at the top, while the vapor off-take is at the bottom.

To maintain a desired temperature gradient over the column when completely within a Dewar tube containing a refrigerant such as liquid air it was obviously most practical to have the temperatures decreasing from the top to the bottom. In addition to the simplicity of construction, the advantage is gained that heat transmission is confined largely to the column itself and there is little heat transfer by convection in the atmosphere surrounding the column.

The column consists of a core, outside tube, and top and bottom heaters. The core was machined from a brass rod, circumferential grooves one-eighth of an inch wide and one-quarter of an inch deep being cut over its full length in such a way as to leave one-sixteenth of an inch thick plates appearing to be strung on a central rod.

A shallow segment was cut from each plate but on opposite sides successively up the column. The core was bored along its axis over the full length to provide a vapor off-take tube from the bottom of the column. The core was tinned and, while hot, inserted into a tinned brass tube serving as the outer wall of the column. Upon cooling, the core and tube formed a substantial unit, the plates with segments removed to permit flow of vapor acting the part of the fractionating column of relatively large surface and long vapor passage.

A brass outlet tube was threaded and sweated into the top of the core and communicated with the central hole. A second brass tube, the inlet tube, was attached to the core in the same manner and communicated with the upper plate. These tubes, which serve to support the weight of the column from the cover plate E and terminate in the standard taper ground joints M, are a principal source of heat entry and should be made of German silver or a similar alloy of low thermal conductivity. They were insulated with cotton wool for some distance above the plate E.

The bottom of the column was closed by a brass plug into which a thermocouple well was machined of such length that the thermocouple was within one-eighth of an inch of the beginning of the vapor off-take tube. Three other thermocouple wells were inserted through the sides of

the column about 2 inches apart as shown. A fifth thermocouple well was drilled into the top of the core and terminated near the top plate. This number of thermocouple wells was necessary to the development of the column and served to show the temperature gradient along its length.

In another column, with slight changes in design, experience has shown that only two thermocouples are essential, although four would be convenient.

Brass tubes each machined with a double thread 16 to the inch were sweated onto the bottom two inches and top two inches of the column. These were coated with shellac, baked, and a double silk covered 30 gage manganin wire wound in a parallel loop in the threads. Copper leads were soldered to the ends of the manganin and passed up the side of the column to terminals on the plate E. The bottom assembly was wrapped in lead foil and a split spring-brass tube fitted over the foil to produce good metallic contact from the inside of the column to the outside of the outer tube. The upper coil was left exposed, being surrounded by a tube one-eighth of an inch larger in diameter and closed at the top and bottom by bakelite disks. These two assemblies served as heaters, the current being controlled by Variac transformers using 24 volt AC in their primary circuits.

Surrounding the upper heater and 1/4 inch away from it was an annular brass cup as shown. It served as a

liquid air container for control of the top temperature and as a means of cooling the top of the column quickly without raising the liquid air level in the Dewar flask above the bottom heater.

The column above the lower heater and below the top heater was wrapped with insulating material and a close-fitting glass tube G closed at the bottom end was slipped on. A layer of infusorial earth, about one-eighth of an inch thick in the bottom of the glass tube, protected the brass closure plate and the thermocouple at the bottom of the column from too direct exposure to liquid air temperature. This insulation was in effect the equivalent of the heater assembly in controlling heat transfer, and was found essential in the production of uniform temperature over the bottom portion of the column.

Thermocouple leads were passed up the column under the insulation to terminals on the bakelite cover-plate E. This plate was supported by three steel rods attached to the bench below. The holes LA through the plate E were for the introduction of liquid air, via glass tubes, as shown. One led to the annular cup at the top of the column and the other led to and terminated at the top of the bottom heater. A Dewar flask D supported on an adjustable pillar (not shown) surrounded the column and its top was fitted through an insulating gasket to the lower

face of the plate E, when in the operating position as shown in Figure 21. In order to keep the plate E free from ice and water, a gentle stream of air was blown across it continuously. This was found necessary to keep the plate E at a reasonably constant temperature as it was used as the cold junction for the thermocouples.

Leads from the heater terminals on plate E were made to the source of current and from the thermocouple terminals to a multiple point rotary switch so that the voltages and hence temperatures could be determined quickly on one potentiometer. The correction for the cold junction at plate E was determined by a thermocouple on the plate surface, whose other junction was in an ice-water mixture.

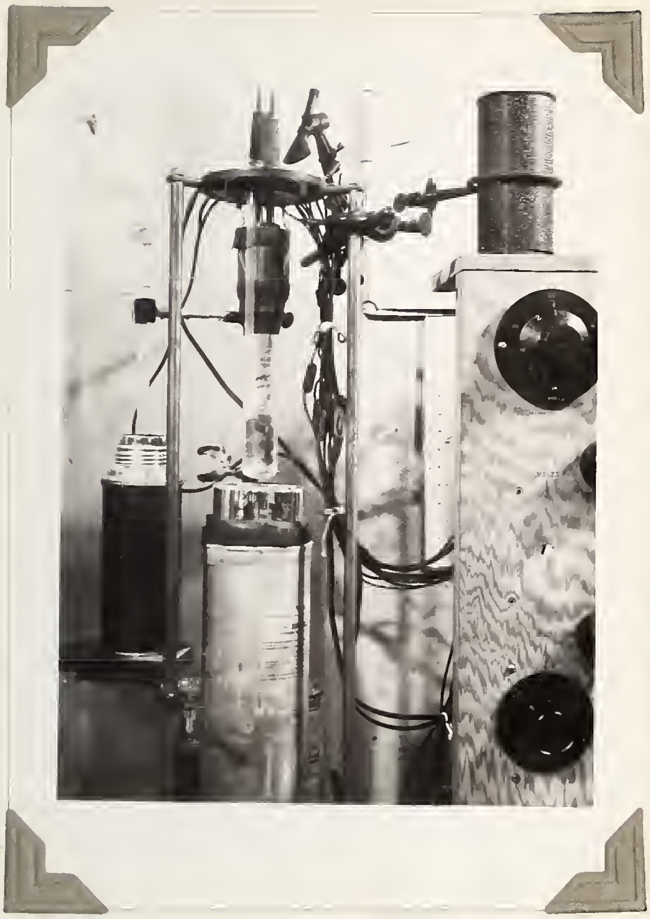


FIGURE 22: The Low Temperature-Low Pressure Fractionating Column.

Operation Calibration and Results

Preliminary to carrying out a fractionation, the column (Figure 9) connecting tubes and accessory apparatus were evacuated. Mercury was allowed to fill the sample burette F and to rise about 3/4 inch above stopcock 16 in the tube through which the sample passes to the column. Stop cock 16 was reversed, the mercury lowered to the mark etched at the bottom of the sample burette, and the pressure and temperature of the gas sample recorded.

With stop cocks 24 and 21 closed, the temperatures along the column were adjusted to the values required for the separation of methane. The level of liquid air was maintained at the top of the bottom heater and small additions to the top liquid air cup were made from time to time. Stop cock 16 was again reversed, and slightly opened to the column. The gas bubbled through the mercury, indicating qualitatively the rate at which it was entering the column. An enlargement in the tube, a few inches above the stop cock, prevented the mercury from being carried over into the column. The gas was permitted to enter slowly as no fractionation took place otherwise.

With stop cock 23 closed, the trap E was cooled with liquid air and stop cock 21 slightly opened until the pressure was equalized. Stop cock 24 was slightly opened to McLeod Gage L_2 and the pressure again equalized. Stop

cocks 21, 23 and 24 were then fully opened and the gas pumped off with the Toepler pump T until the pressure in the column read 1 mm. The diffusion pump H was then operated in conjunction with the Toepler until the pressure remained constant at 0.25 mm. of mercury. The amount of methane and nitrogen was measured in the fraction receiver R by means of the manometer M_2. Due to the small mass of gas in each fraction it was found impractical to determine the nitrogen content of the first, or methane-nitrogen fraction, by means of density determinations. Combustion in the Orsat apparatus was therefore resorted to.

With stop cocks 21 and 23 closed the temperatures along the column were adjusted for ethane, then stop cock 21 was opened and the gas distilled over into the liquid air trap E. When the McLeod Gage showed a pressure of 0.10 mm. of mercury in the column, for three successive readings with stop cock 21 closed, distillation was discontinued. The liquid air was removed and the ethane pumped off with diffusion pump H and Toepler pump T and measured. The same procedure was repeated for each of the heavier gases after the correct temperature distribution had been established in the column.

After the butanes had been removed and measured the column was allowed to warm up and the pentanes plus any heavier hydrocarbons pumped off and measured as vapor.

The amount of pentanes plus was generally very small and frequently the McLeod Gage was used to read the pressure in the fraction receiver.

To complete one run required about two and one-half hours for a lean gas and three hours for a rich gas. Liquid air consumed per run averaged about three pounds.

In the development of the technique of operation with the column the primary variables observed and adjusted were the temperatures, as measured by the five thermocouples, and the pressure on the outlet side of the column, as measured by the McLeod Gage. In addition, the pressure in the fraction receiver showing the process of distillation was of importance in development work using mixtures of known composition. The work of Ward(49) in determining suitable cut temperatures for his apparatus was of great value in providing a guide to be followed in fixing the lowest or vapor off-take temperature.

The procedure adopted in testing the column was to set the vapor off-take temperatures; i.e., TC 1, at the temperatures listed by Ward for the fourth fractional condenser in his train. Attempts were made to maintain the top of the column; i.e., TC 2, at the temperature given by Ward for his first condenser. This was not possible and also found to be unnecessary. In practice,

it was found only necessary to maintain TC 5 somewhat below the temperature set by Ward for his first receiver, and TC 2 the same or warmer. The result was a satisfactory temperature gradient down the column to the fixed bottom temperature.

After some experience with the column on mixtures of known composition, and some minor adjustments, the following results were obtained:

Volume Percent

	Mixture #3 as Prepared	Found		
		1	2	3
Methane	53.73	53.43	53.56	53.70
Ethane	24.21	24.36	24.14	24.29
Propane	13.53	13.36	13.40	13.62
Butanes	8.53	8.85	8.90	8.39

	Mixture #4 as Prepared	Found	
		1	2
Methane	48.25	48.17	48.21
Ethane	21.71	21.92	21.77
Propane	12.15	12.06	12.12
Butanes	17.89	17.85	17.90

The following are typical duplicate analyses of two rich and two lean gases after the technique for operation had been well developed:

	Gas "A" Vol.%		Gas "B" Vol.%	
Analysis No:	1	2	1	2
Methane + N_2	62.40	62.40	54.60	54.67
Ethane	17.93	17.90	16.69	16.77
Propane	12.64	12.76	15.25	14.96
Butane	6.13	6.05	12.98	12.97
Pentanes +	0.90	0.89	0.48	0.63
	100.00	100.00	100.00	100.00

	Gas "C" Vol.%		Gas "D" Vol.%	
Analysis No:	1	2	1	2
Methane + N_2	93.30	93.29	92.08	92.03
Ethane	4.86	4.86	5.77	5.71
Propane	1.25	1.28	1.56	1.52
Butane	0.45	0.46	0.48	0.64
Pentanes +	0.14	0.11	0.11	0.10
	100.00	100.00	100.00	100.00

The results given below on the analysis of Royalite Gas at periods of several months apart are an indication of the reliability of the analysis and technique before it reached its present stage of development.

	Vol. % as at Dec. 1/39	Vol. % as at Mar. 25/40
Methane + N_2	84.74	84.62
Ethane	9.35	9.44
Propane	4.03	4.05
Butane	1.56	1.58
Pentanes +	0.32	.31
	100.00	100.00

The cutting pressures used at all times were those set by Ward. These were 0.25 mm. of mercury for Methane, and 0.10 mm. of mercury for all other gases. Cutting temperatures for the fractions are listed in the following table, together with the number of the thermocouple. The temperatures, in degrees Centigrade, listed, are those at which separation of the individual component from the rest of the gas takes place.

TABLE - II A

Gas	TC 1	3	4	5	2
Methane + N_2	-175	-169	-164	-150	-119
Ethane	-160	-154	-145	-135	-109
Propane	-142	-134	-	-120	-100
Butane	-117	-	-	-100	- 74

Thermocouples 3 and 4 were used to check the temperature gradient during the calibration of the column and were seldom used afterwards. Thermocouple #3 is very useful, however, in following the initial cooling of the column and should be retained. Due to the construction of the column, the changes in temperature at the top were greater and less readily controlled than at the bottom points. Variations up to 10° C. in the temperature of TC 2 did not, however, affect the results of fractionation as long as TC 5 was maintained close to the temperature listed; a requirement easily achieved. Thermocouple #4 could be discarded without loss. For the methane plus nitrogen cut, the temperature of TC 1 could be between -172 and -175° C. The other cut temperatures and the temperature of TC 5 as listed were maintained to within 1° C.

A few attempts were made to separate n-butane and i-butane but without success. As such a separation was not required in connection with the work described previously, no further attempts were made to effect this separation. It is hoped, however, that when time permits, a technique may be developed that will give a separation of n- and i-butane. The small vapor pressure ratio of the butanes at the temperatures used (see Table 11), makes it highly improbable that the present technique will suffice.

It should be pointed out that no separation of nitrogen and other non-condensible gases from methane was attempted. Orsat analysis of the methane fraction provided the information desired and in the present case, a thermal conductivity method may be used. However, it is quite probable that separation in the column is possible and the problem will be investigated. The apparatus and method may be adapted easily to hydrocarbon mixtures with other common gases when used in conjunction with an Orsat apparatus. Further, if olefines are present, they may be removed as shown by Ward(49) with the corresponding paraffin and determined by absorption in the usual way.

Discussion

The results given are not exceptional in any way and have been repeated many times on a variety of gas mixtures. The close agreement between duplicate analyses as illustrated here is superior to that obtained in other methods of analysis with the possible exception of that due to Ward.

The dependence to be placed on the results is illustrated in the discussion of the development of the method by analysis of gas mixtures of known composition. The agreement found there is as good as the accuracy with which the known mixtures were made. The slightly better agreement among duplicate analyses suggests that they give a truer analysis of the mixtures.

The analyses were calculated on the basis of the sum of the volumes of all the components taken off and not on the volume of sample initially taken. The total volume off, calculated to the input pressure of the sample was always slightly larger than the actual input volume; usually 0.2 to 0.4% larger. The sample was measured at about 60 cm. of mercury pressure and the fractions off at 30 cm. of mercury, or less. The discrepancy between the sample volume and the total volume off may be wholly accounted for by the deviation of the initial sample from the ideal gas laws. The fractions were measured under more

nearly ideal conditions and hence the analyses, as calculated, are closely molecular percentages.

As a result of present experience, several problems arise which may be solved by modifications in a future design. Considerable trouble was experienced in the initial cooling of the column to the temperatures required for methane separation. This may be due partly to heat losses which can be reduced by using German silver inlet and outlet tubes and dispensing with the air space between the top heater and the annular liquid air cup. As was pointed out in the operation, only four thermocouples were necessary, and TC 4 can be dispensed with.

Summarizing the performance of the apparatus and the value of the method in the analysis of mixtures of paraffin hydrocarbons, the following points may be mentioned:

1. The time required for one analysis is exceptionally short, approximately 2.5 hours.

2. The liquid air consumed per analysis is low, approximately three pounds.

3. A small gas sample, usually 85 c.cm. but ranging from 50 to 150 c.cm. more or less, is sufficient for a precise analysis.

4. The apparatus is relatively simple, inexpensive, and the technique of operation readily learned.

5. The results are highly accurate, analyses in duplicate agreeing to 0.03% in lean gases and 0.1% in rich gases.

APPENDIX II

Molecular Weights

In work on petroleum oils such as is being done in this laboratory, it is desirable to know the mean molecular weights of liquids and liquid fractions. The ordinary methods are too time-consuming, are not entirely reliable on single determinations, and require larger quantities of material than are sometimes available; therefore some other means which is more rapid, more reliable, and useful on small quantities is desirable. Steed(47) has attempted to show that there is a direct relationship between the mean molecular weight of certain oils and their density or refractive index. This work was extended by Piercey(31), working in this laboratory, to Turner Valley naphthas. The present work has the same object in view.

In this work it was desirable to know the mean molecular weights, densities, and refractive indices of the following materials: Royalite naphtha; fractions from A.S.T.M. distillation of Royalite naphtha; liquid condensates from the solubility pipettes.

Use was made of the well known equation: -

$$M_2 = K \frac{W_2 M_1}{\Delta T W_1}$$

Where:

M_1 = Molecular weight of solvent.

M_2 = Molecular weight of solute.

W_1 = Grams of solvent.

W_2 = Grams of solute.

ΔT = Depression of the freezing point.

K = Cryoscopic constant for the solvent.

Nitrobenzene was used as the solvent. It was purified by recrystallization until no change took place in its freezing point. The cryoscopic constant was determined experimentally using the following purified solutes: benzene, cyclohexane, n-heptane.

Rearranging the equation we get: -

$$K = \Delta T \frac{M_2 W_1}{M_1 W_2}$$

A value for K was obtained for each of three additions of solute to the same sample of solvent. The above equation is based on the assumption that the solutions are ideal, that is to say, in practice, infinitely dilute. The equation applies only at infinite dilution and K is calculated from a series of measurements on solutions of finite concentrations. The values of K were plotted against concentra-

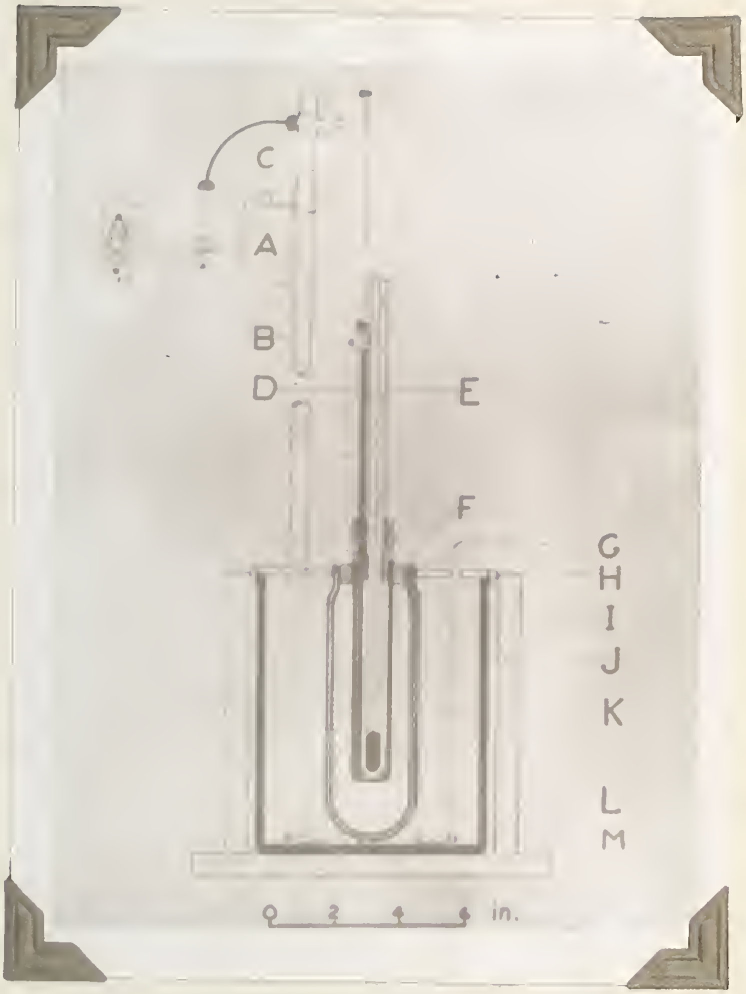


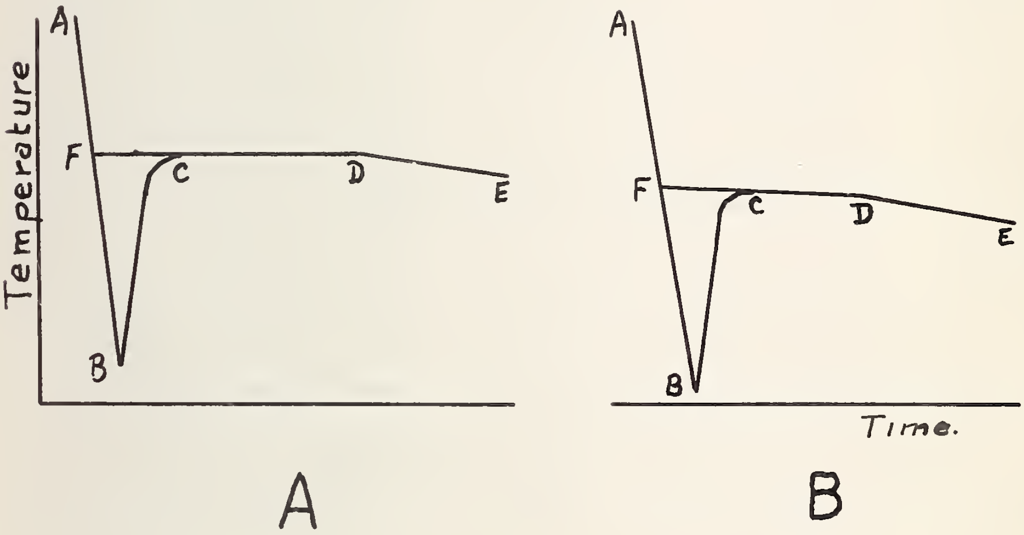
FIGURE 23: Diagram of Molecular Weight Apparatus.

tion and the best straight line through these points projected back to infinite dilution. This line may be safely assumed to be straight due to the small change in concentration of solute even with the addition of three samples of solute to the same mass of solvent. This procedure was repeated for each of the solutes. The cryoscopic constant at zero concentration for all three solutes was almost identical. The value used was 56.2.

The apparatus was of the Beckmann type in the modification used by Piercey(31). This was changed in certain details and used by the authors in the work. The manually operated stirrer in the cooling bath was replaced by a mechanical stirrer. The single ring stirrer in the freezing point tube was replaced by a double ring stirrer; the second ring being about 3 cm. above the other. An electrical vibrator was attached to the Beckmann thermometer to replace tapping by hand. A special pycnometer with ground glass caps was made. It held enough solute sample for only one addition. The outlet tip of this pycnometer was a fire-polished tube about 6 mm. in length, 2.5 mm. outside diameter, and 1 mm. inside diameter. This eliminated the tendency of the naphtha to leave a hanging drop on the tip of the pycnometer after discharge, with consequent loss of material and error in weight.

About 35 grams of nitrobenzene was used. To this was added about 2 grams of anhydrous magnesium per-

chlorate as a drying agent. Freezing point determinations were made by use of the temperature-time plot or cooling curve as applied by Steed(45) in his work on petroleum fractions. For a pure solvent, the cooling curve was of the type illustrated in A below. For solutions the curve was of type B.



The point F, obtained by extrapolation of CD back to AB was taken as the correct freezing point. A detailed interpretation of these curves is contained in Piercey's thesis and will not be repeated here.

Freezing point determinations were made on the pure solvent until two successive values agreed to 0.002° C. Single freezing point determinations were made on the solutions after each addition of solute. The mean molecular weights determined, together with refractive

index and density are given in Table 12 and are shown graphically in Figure 25.

TABLE 12

Royalite Naphtha

Refractive Index	1.3955
Density	0.7009
Mean Molecular Wt.	93.7

A.S.T.M. Fractions

Fraction	Temp. Range	Vol. cc.	Refractive Index	Density	Mean Mol. Wt.
1	to 70°C	20	1.3826	0.6726	87.5
2	70-81	20	1.3880	0.6839	90.5
3	81-90	20	1.3945	0.6972	91.5
4	90-98	21	1.4007	0.7104	93.1
5	98-110	21	1.4087	0.7259	99.8
6	110-150	18	1.4208	0.7481	111.5

Residue - 1cc.

Loss - 4cc.

Condensate Residues From Solubility Pipettes

No.	Pressure		Refract. Index	Density	Mean Mol. Wt.
	lbs/sq.in.	Atmos.			
1	314.6	21.41	1.4063	0.7238	98.7
2	314.6		1.4055	0.7228	97.0
3	513.6	34.95	1.4055	0.7216	98.9
4	1013.6	68.97	1.4055	0.7226	97.2
5	1013.6		1.4055	0.7219	-
6	1313.6	89.38	1.4065	0.7230	-
7	1313.6		1.4065	0.7230	-

DISCUSSION

The naphtha consisted largely of saturated hydrocarbons with small amounts of aromatics and cycloparaffins. This may account for the shape of the molecular weight curves, which would be continuous if the naphtha consisted entirely of paraffins. It is thought that the first two fractions consist largely of pentanes and hexanes followed by the fractions relatively rich in aromatics and cycloparaffins. The latter have a higher density and refractive index due to their relatively low molecular volume and high polarity. Thus, as is evident in Figure 25, the density and refractive index increase rapidly without much increase in molecular weight until the bulk of the aromatics and naphthenes has been removed. Above a molecular weight of 95 the fractions become almost entirely paraffinic in character due to the large percentage of saturated hydrocarbons. Ring compounds which may be present in small amounts have probably aliphatic side chains thus increasing their resemblance to the paraffins.

The location of the naphtha points with respect to the mean molecular weight curves may be explained on

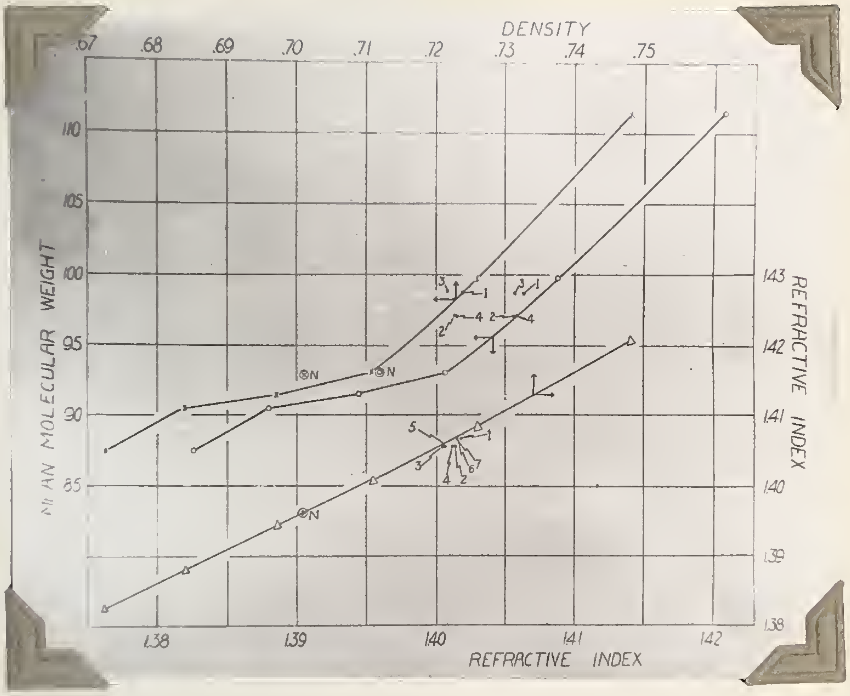


FIGURE 25: Mean Molecular Weight, Refractive Index and Density of Royalite Naphtha and its Fractions.

Legend

Mean Mol. Weight-Density ——X—— X

Mean Mol. Weight-Refractive Index ——O—— O

Refractive Index-Density ——Δ—— Δ

The figures on the face of the graph refer to the condensate residues listed in Table 12.

the basis of the composition of the whole naphtha compared to its fractions. The high content of the lower paraffins, pentanes and hexanes (about 40%), effectively masks the action of the ring compounds in tending to show relatively high density and refractive index. In fractions 3 and 4 there is a concentration of ring compounds and their effect is enhanced compared to their effect in the whole naphtha. Consequently, in this case, the points for the naphtha would be expected to fall to the left of the line. Another case where the naphtha was much less volatile and of higher mean molecular weight, but containing no more ring compounds, the points would appear close or possibly to the left of the upper part of the curve.

The naphtha point falls on the Refractive Index-Density line as would be expected. These properties parallel one another closely, regardless of molecular weight, in that they measure much the same thing, molecular volume. The almost straight line relating refractive index to density indicates the close relationship between these properties. Whereas molecular volume and molecular weight may be parallel in one series, they are not in comparing for example aromatics with paraffins.

The condensate residues from runs at pressures between 21.4 and 89.4 atmospheres are indicated by numbered dots. It should be pointed out that these residues

TABLE 13

Comparison of mol weights of condensates from refractive index curve with mol weights based on pentanes by distillation and mol weight of residue.

Exp.No.	19	20	27	21	23	24	26
No. on Fig.25.	1	2	3	4	5	6	7
Meas. M.W. Cond. Res.	98.7	97.0	98.9	97.2	97.0	97.7	97.7
V% C_5H_{12} in Cond.	18.2	13.1	12.1	15.2	14.8	16.0	14.3
r_C Cond.	1.3947	1.3951	1.3975	1.3947	1.3979	1.3960	1.3950
d Cond. Fig.25.	0.6975	0.6985	0.7035	0.6975	0.7045	0.7026	0.6985
M.W. Cond. Fig.25.	91.5	91.6	92.2	91.5	92.3	91.8	91.6
M.W. Cond. Calculated	91.2	91.9	94.2	91.6	92.5	92.4	92.2

NOTE:

In experiments 23, 24, 26, the refractive index of the condensate residue was measured and its mean molecular weight taken from Fig. 25. It was not measured directly as was the case in the other experiments. The calculated mean molecular weight of the condensate therefore becomes, in these cases, a test only of the accuracy of the fractional distillation for pentanes.

have been stripped of their pentanes before molecular weights, densities and refractive indices were determined. Very little change in the molecular weights of the condensate-residues took place over the range of pressures used. Transfer of pentanes to the gas phase, with practically no transfer of hexanes or higher hydrocarbons, is suggested by the close proximity of all the points to the same molecular weight.

Due to the small amount of data obtained on this portion of the work it must be interpreted in a strictly qualitative manner. It may be of interest, however, to consider some comparisons which have been made from the available data. (Table 13).

The mean molecular weights of the condensates were computed from the known mean molecular weights of the residues and the measured pentane content of the condensates. For comparison with the graphical method based upon density or refractive index, the mean molecular weight of the condensate was read from Figure 25. The results obtained check well, even though the mean molecular weights fall on that part of the curve where the concentration of cyclic compounds is considered to be high, and where poorer agreement than has been obtained might be expected. The molecular weights of these condensates differ very little from one another, hence test

the application of this method within a very limited part of the curve. As the main project is continued over a wider range of pressures, condensates of higher and lower mean molecular weights will be obtained and more information of a quantitative nature will be added to this phase of the work.

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